

STUDY OF TUNDISH WORKING LININGS

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ABSTRACT

Many projectable refractory materials based on magnesia silicate developed by several suppliers are being used by the steelmaking industry, particularly as working lining for the continuous casting tundish.

With the aim of having an insight on the chemical stability of magnesia silicate based materials in front of liquid steel containing Mg and Si, a thermodynamical analysis of equilibrium was carried out.

According to the results and taking into account a review of literature, tests were run in a slab caster in order to evaluate both refractory lining and steel. Post mortem study of samples as well as inclusion analysis and silicon reversion study, were carried out. Results and conclusions are presented.

Key words: magnesia silicate, tundish lining, liquid steel, equilibrium, inclusions.

INTRODUCTION

The tundish has a key role in casting operations, as fluid flow, heat transfer and chemical reactions taking place within it have strong influence on quality of steel delivered to the molds.

One of the main variables to be taken into account is the tundish working lining material in contact with liquid steel. Most of the steelshops use for this purpose basic materials including more than 80 % of MgO.

In order to study an alternative refractory material based on forsterite a thermodynamical analysis of equilibrium between this material and liquid steel was carried out. Then tests were run in a slab caster, in order to evaluate lining behavior, influence on inclusion population and possibility of silicon reversion, important for low silicon steel grades.

INTERACTION BETWEEN REFRACTORY AND LIQUID STEEL

To analyze stability of forsterite and periclase in front of a liquid steel bath containing dissolved Mg and Si in solution, the Fe-Si-Mg-O system was studied at different temperatures.

Thermodynamic data presented in table 1 were taken as base for the study. Equations corresponding to equilibrium between periclase and forsterite, and forsterite and silica were

developed. Based on those equations, equilibrium diagrams shown in figures 1 and 2 were built.

These equilibrium diagrams show the stability fields of the oxide phases (periclase, forsterite and silica), depending of Mg and Si dissolved in liquid steel, at three different temperatures. Even though values of dissolved Mg larger than 5 ppm are not common, they are taken into account for the sake of completeness.

These graphics were built based on the consideration that all phases present in the system are in solid state, what is true up to 1550°C. Anyway, the presence of liquid over that temperature occurs between the stability fields of silica and forsterite. This region, as seen below, is not relevant for the steel grades surveyed in this work, except for the case of very low Mg content and very high steel temperature.

When comparing figures 1 and 2 it is clear that as temperature increases, the field of stability of forsterite is enlarged, related to that of the periclase.

Two different steel grades were taken into account: LCAK (0.04% Si max) and structural steels (0.15 to 0.40% Si). It is supposed, based on literature and previous experience, that normal values of Mg dissolved in the steel range from 0 to 6 ppm and that in abnormal or localized situations it could reach up to 15 ppm.

According to figure 3, a forsterite refractory will be stable at 1550°C, in front of LCAK steel with 2 ppm Mg, as long as Si is not less than 0.01%. For max Si content, equilibrium is yet possible with higher Mg, 4 ppm max. At 1600°C, forsterite will be stable in front of LCAK steels with 2 ppm Mg even for very low Si content (see figure 4).

When looking to structural steels (0.15 to 0.40 %Si), forsterite is stable at 1550°C or 1600° C even for high Mg content (figures 5 and 6).

3. PLANT TESTS.

According to results of thermodynamical analysis and of a literature review on application of refractory materials based on magnesia silicate, a test was designed and carried out at a slab caster. The refractory material had 61 % MgO and 19 % SiO₂. Behavior of material in service and interaction with steel were evaluated through the first seven heats of a sequence of LCAK steel.

Samples were taken for liquid steel in the tundish as follows:

- ♦ Sample 1. 10 minutes after heat start.
- ♦ Sample 2. 20 minutes after heat start.
- ♦ Sample 3. 30 minutes after heat start.

Steel chemical analysis was carried out on samples 1 and 3 of each heat. Light microscopy and EDS analysis of inclusions was carried out on sample 2 of each heat.

In the next paragraphs, temperature evolution, silicon reversion, inclusion chemistry and post mortem study of refractories is detailed.

4. TEMPERATURE OF LIQUID STEEL IN THE TUNDISH.

Figure 7 shows temperature variation of the liquid steel in the tundish along the seven heats, compared with another seven heats of a normal magnesia lining.

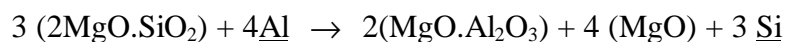
Temperature loss seems to be larger for forsterite lining than for normal magnesia lining for the first three heats, but after that the thermal behavior of forsterite is better than that of the magnesia lining. This later behavior is what was expected based on thermal conductivity values for both materials. Difference in tundish preheating could account for the behavior in the first heats.

5. SILICON REVERSION.

The evolution of Si content along the seven heats, both in ladle furnace and #1 and #3 tundish samples can be observed in figure 8. Figure 9 shows same data for a sequence with normal magnesia lining. It can be concluded that there was no silicon reversion to the steel, related to the use of forsterite as tundish lining, as curves corresponding to first and final tundish sample are overlapped.

Bannenberg and Lachmund [3] carried out laboratory tests involving contact between steel with no silicon with refractory materials with different silica contents. They proved that silicon increase in liquid steel does not depend upon silica content in the refractory material as far as SiO₂ content is less than 40% (figures 10 and 11).

The increase in silicon content in liquid steel is produced up to reaching equilibrium according to the following equation:



So the amount of silicon that reverts to the steel is a function of aluminum content in the steel. Kinetics of this reaction is governed by the following equation:

$$\Delta Si = k \sqrt{t} \quad \text{Where } k = \text{equilibrium constant; } t = \text{time.}$$

5. INCLUSIONS.

EDS analysis and size of some typical inclusions found in tundish samples is presented on table 2. Just one macroinclusion was detected on each sample. On three samples, they were manganese alumina silicates, probably coming from reoxidation by contact with air. On one other sample the macroinclusion was calcium magnesium alumina silicate, probably coming from slag.

Microinclusiones were normal calcium aluminates, containing some magnesia, typical of this steel grade. So, no influence on inclusion chemistry was detected coming from the forsterite tundish lining.

6. POST MORTEM STUDY.

A post mortem study was carried out to have an insight of the profile of steel and slag attack on the lining. Samples were taken after the aforementioned sequence of 7 heats of LCAK steel ended. The samples were polished and observed with magnifying glass, in a light microscope and in a SEM. Chemical analysis, EDS and X Ray Diffraction were performed to assess structure, chemical attack, etc.

Main phases found in the forsterite lining were periclase, forsterite, calcium-magnesium-alumina silicate, magnesioferrite and α quartz. This one could be reduced by Ca and Al dissolved in the steel. When analyzing equilibrium for Si/SiO₂/O₂ and C/CO/O₂, silica will be stable up to 1667°C.

The profile of attack can be described as the reaction of the magnesium -calcium silicate with aluminum and calcium dissolved in the steel, or alumina and calcium oxide present in the slag. The reaction products are spinels, calcium silicates and alumina calcium silicates of low melting point. They give place to certain amount of liquid at working temperatures and they react, first with forsterite grains, then with periclase grains (Figures 12, 13 and 14). EDS analysis of lining matrix at different depth from the hot surface is presented on table 3.

Spinel in contact with the slag had less MgO than those in contact with the steel. So these latest ones are probably formed at higher temperature, as MgO solubility in alumina is high just at high temperatures.

The working lining did not sinter against the permanent lining, making tundish cleaning easier. There were some 7 to 10 mm not sintered. The safety lining was in good shape.

7. CONCLUSIONS.

Forsterite based tundish lining was studied from thermodynamical point of view and plant tests.

Thermodynamical analysis revealed that forsterite is stable in contact with liquid steel for structural purposes, containing 0.15 to 0.40 %Si, and normal amounts of dissolved Mg. Nevertheless, for LCAK steels containing less than 0.04% Si, either forsterite or periclase is the phase in equilibrium, depending on temperature, Si content and Mg content.

Temperature loss of liquid steel in the tundish was lower for forsterite lining than for magnesia lining, for the fourth heat and the following ones. For the first heats, it looked like the preheating had more influence than the lining type. Further tests and thermal modeling are interesting to get final conclusions with regards to this important issue.

Forsterite lining did not give origin to silicon reversion, a critical phenomenon for certain LCAK grades with Si max 0.03%. The results were quite similar to those obtained with

magnesia lining. Besides, no influence was detected on macroinclusion and microinclusion chemistry.

The working lining did not sintered against the permanent lining. Main phases found in the forsterite lining were periclase, forsterite, calcium-magnesium-alumina silicate, magnesioferrite and α quartz. There was a reaction of the magnesium -calcium silicate with aluminum and calcium dissolved in the steel, or alumina and calcium oxide present in the slag. The reaction products are spinels, calcium silicates and alumina calcium silicates of low melting point. They give place to certain amount of liquid at working temperatures and they react, first with forsterite grains, then with periclase grains.

So the results were encouraging in order to continue with the use and study of these materials for tundish lining.

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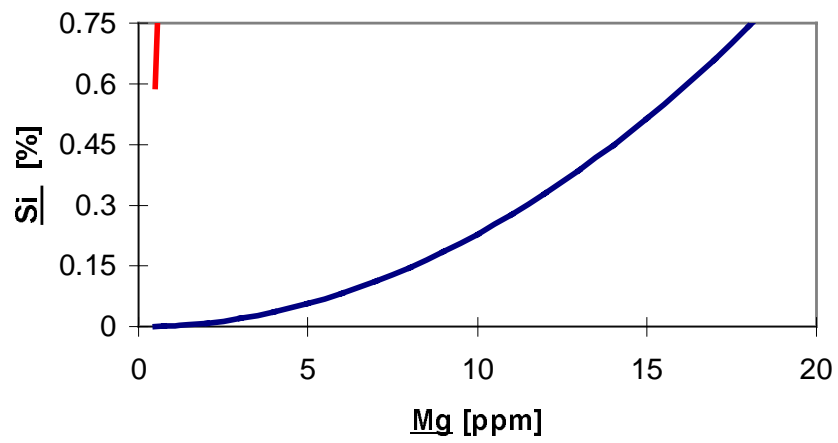


Figure 1: Equilibrium in the system Fe-Si-Mg-O at 1550 °C.

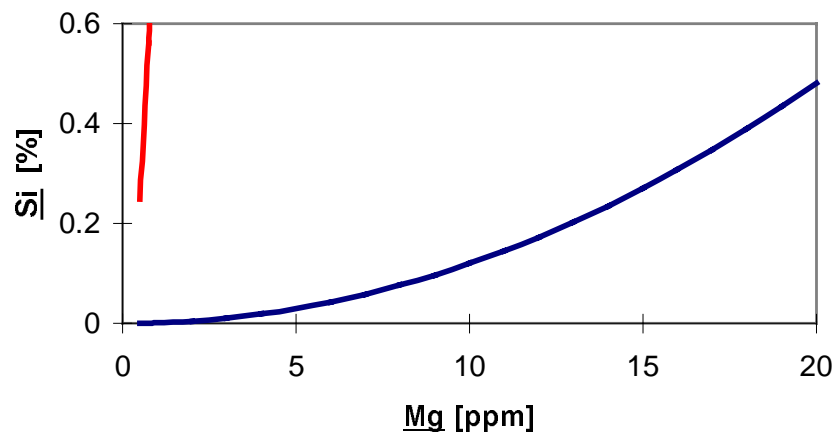


Figure 2: Equilibrium in the system Fe-Si-Mg-O at 1600 °C

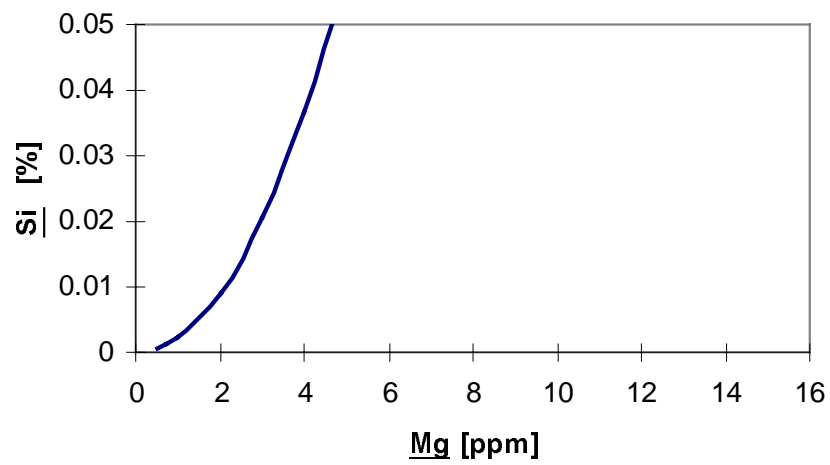


Figure 3: Equilibrium in the system Fe-Si-Mg-O for LCAK steels at 1550 °C.

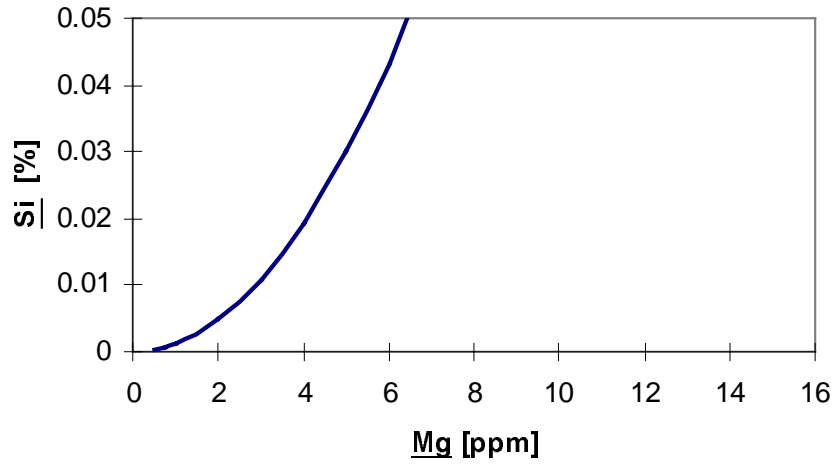


Figure 4: Equilibrium in the system Fe-Si-Mg-O for LCAK steels at 1600 °C.

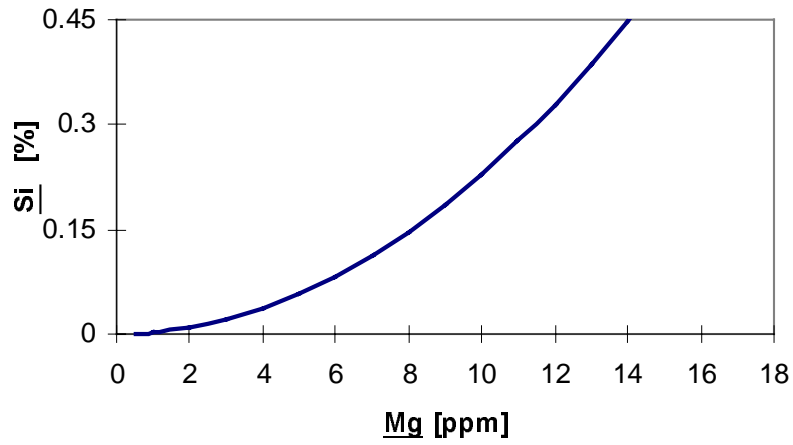


Figure 5: Equilibrium in the system Fe-Si-Mg-O for structural steels at 1550 °C.

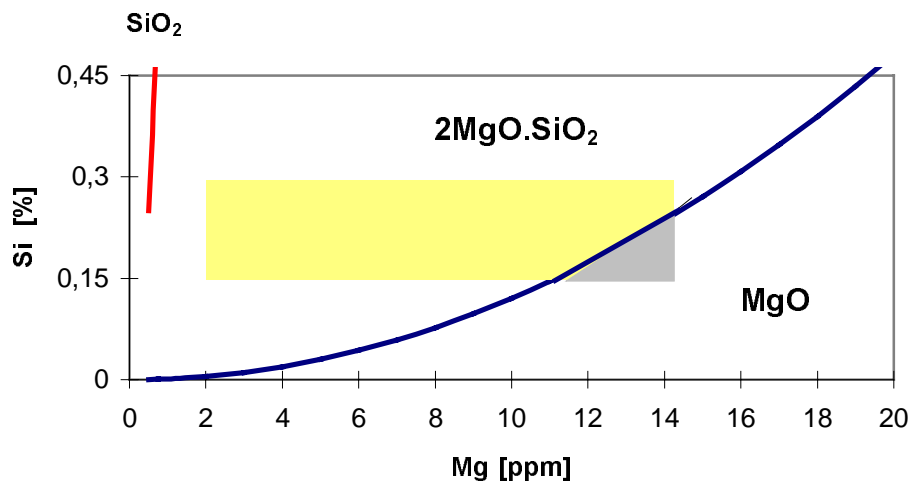


Figure 6: Equilibrium in the system Fe-Si-Mg-O for structural steels at 1600 °C.

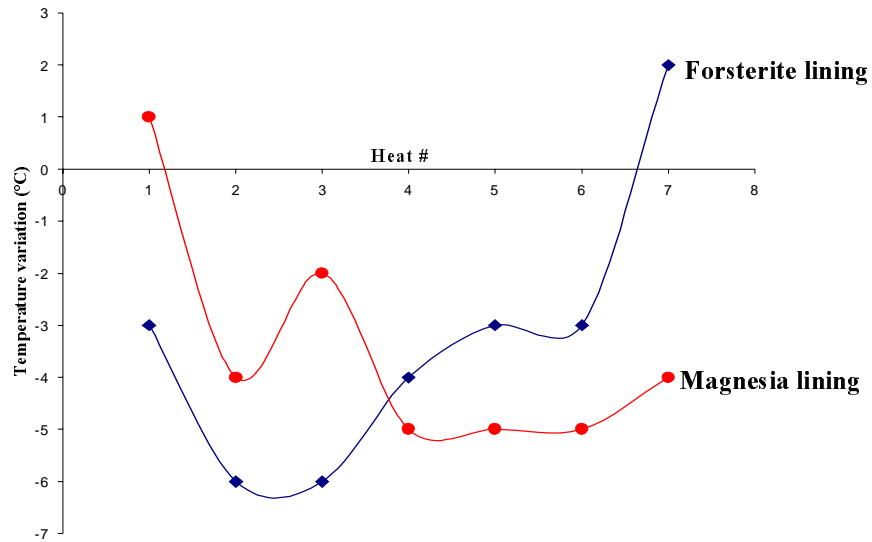


Figure 7: Liquid steel temperature variation along the first seven heats of a sequence, with magnesia lining and with forsterite lining.

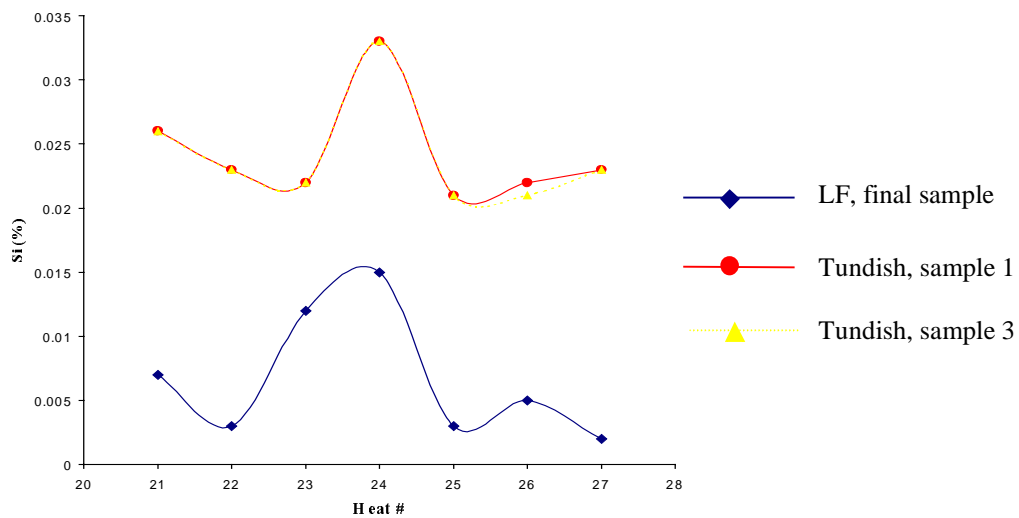


Figure 8: Evolution of Si content in liquid steel, during the first seven heats of a sequence (forsterite tundish lining).

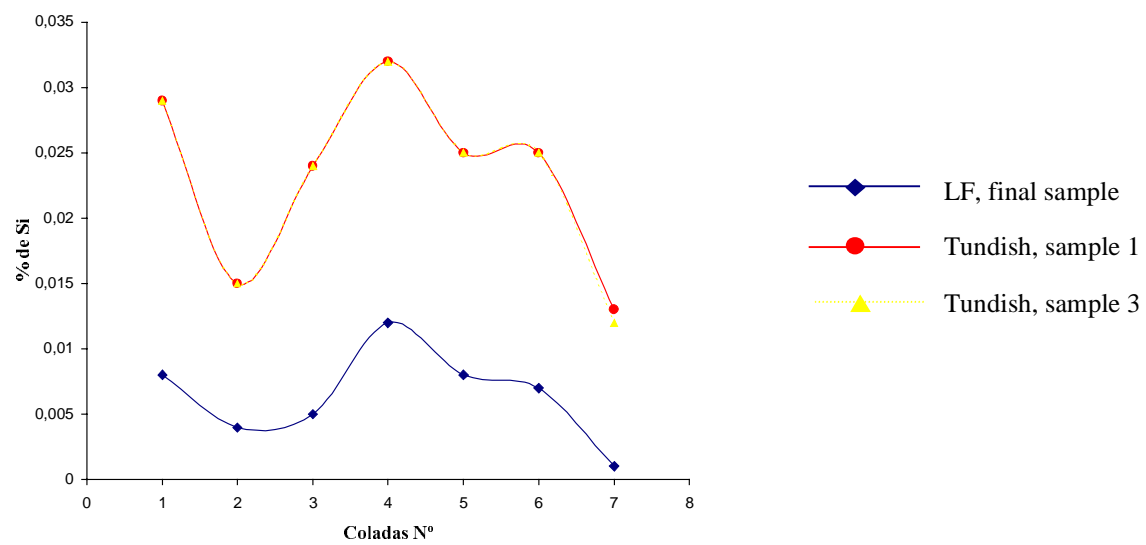


Figure 9: Evolution of Si content in liquid steel, during the first seven heats of a sequence (magnesia tundish lining).

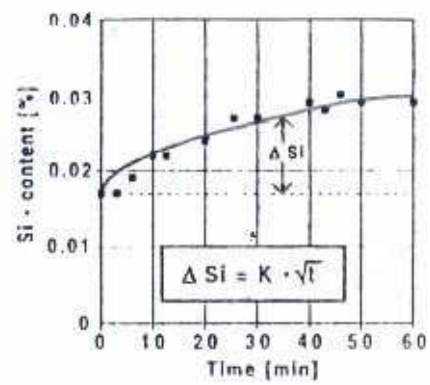


Figure 10: Increase of silicon content in the steel [3].

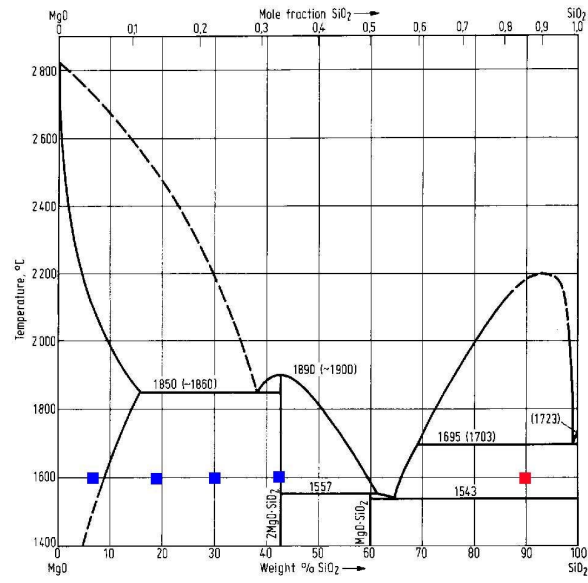


Figure 11: Refractory materials tested by Lachmund and Bannenberg[3]

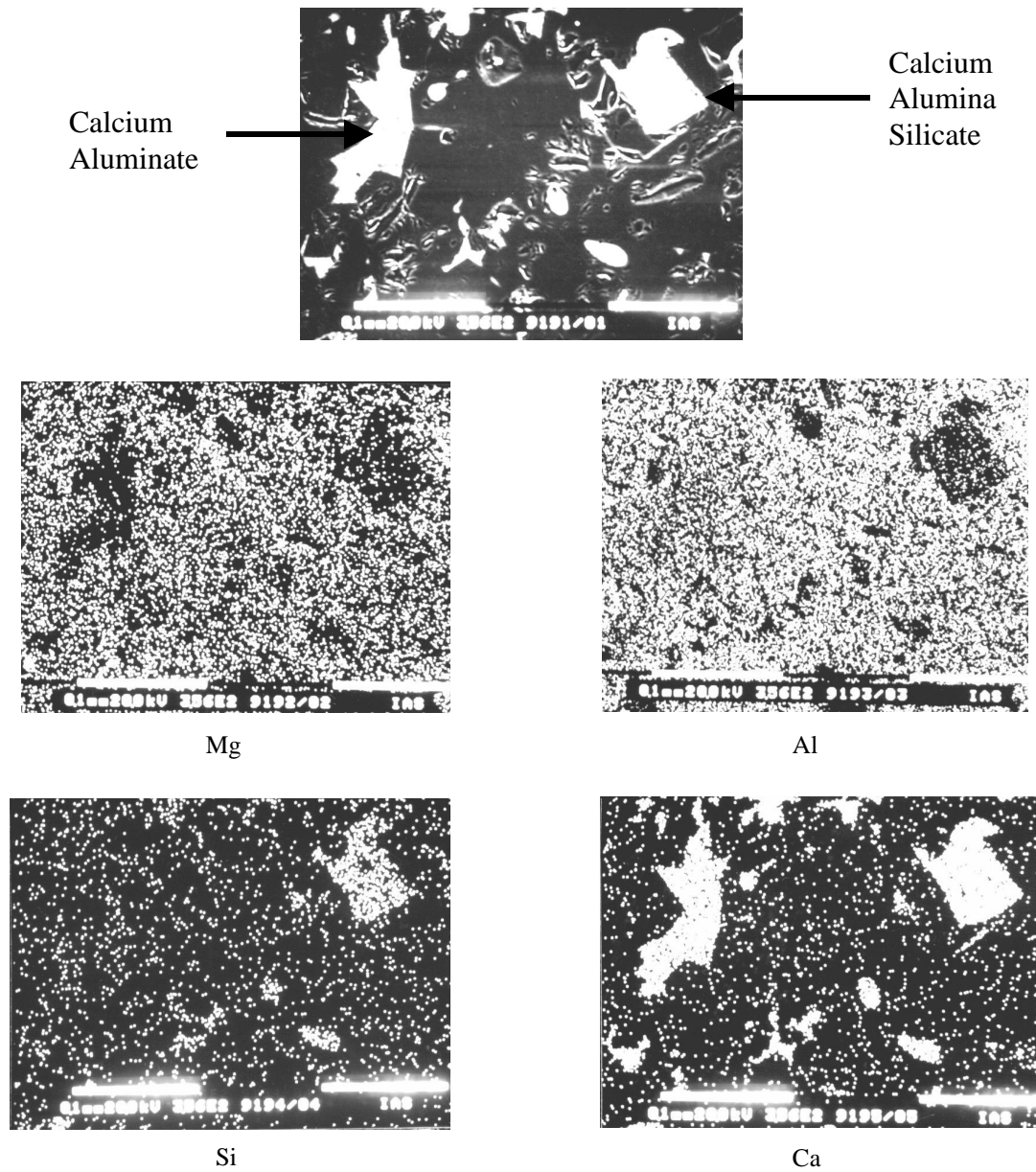
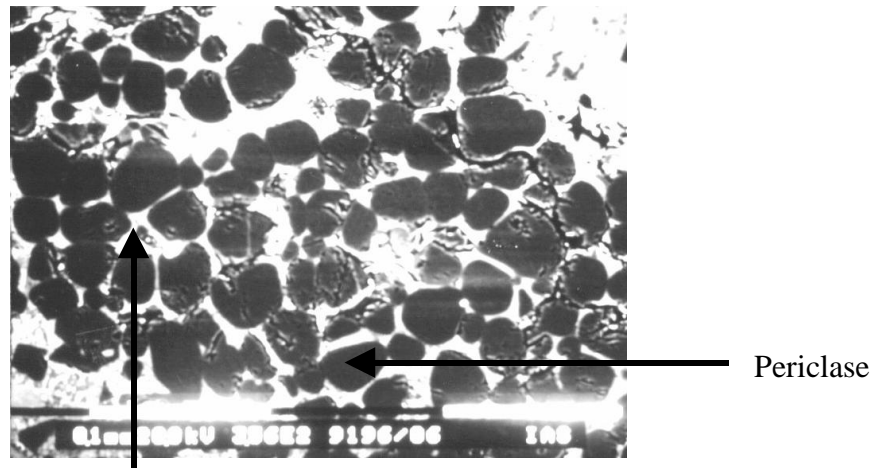
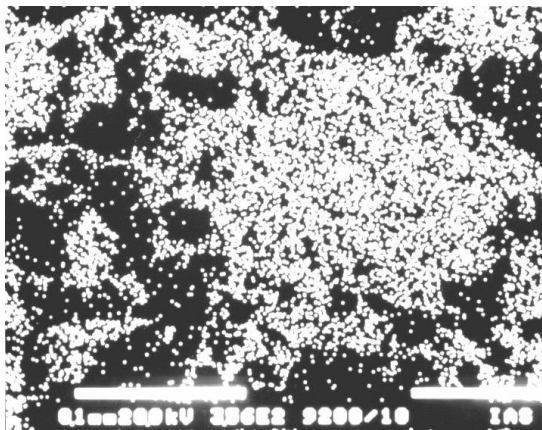
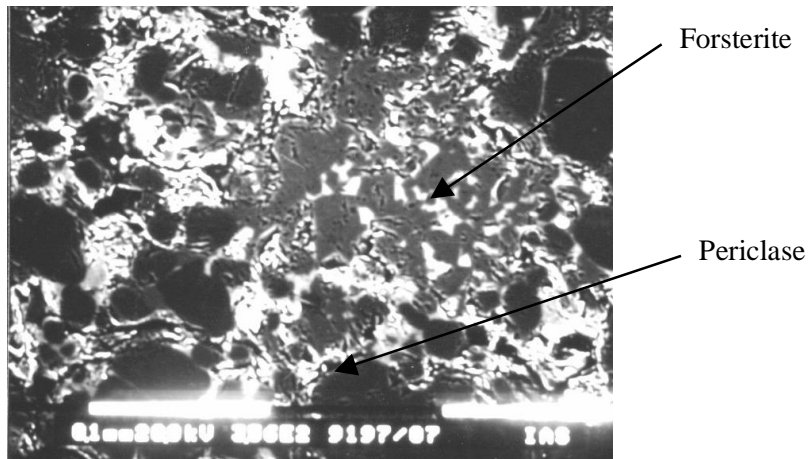


Figure 12: SEM image and mapping for forsterite lining at 1 mm depth from the hot surface.

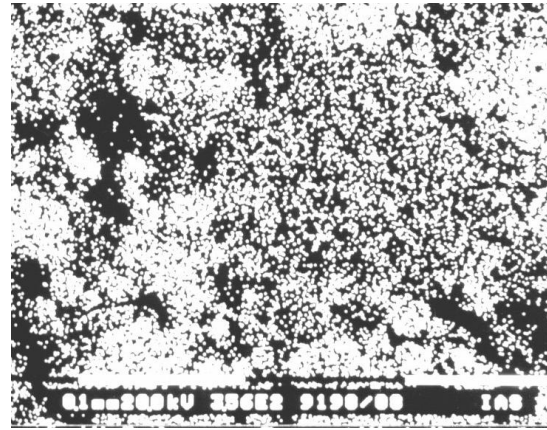


Calcium Alumina Silicate: Al_2O_3 18 %; SiO_2 38 %; CaO 40 %.

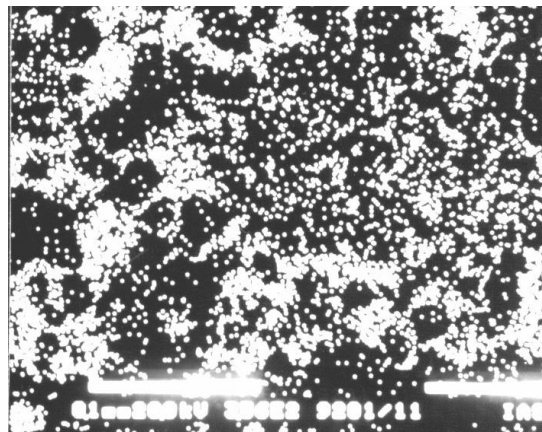
Figure 13: SEM image and EDS analysis of a sample of forsterite lining at 2 mm depth from the hot surface.



Mg



Si



Ca

Figure 14: SEM image and mapping at 7 mm depth from the hot surface.

Table 1: Free energy of formation for 2MgO.SiO₂, and solubility products for MgO and SiO₂ in liquid steel.

Phase	Thermodynamic data	Reference
2MgO.SiO ₂	$\Delta G^\circ = -15,100 + 0.0 T$	[1]
MgO (s)	$\log K = -26,11/T + 8.24$	[2]
SiO ₂	$\log K = -31,04 /T + 12$	[2]

Table 2: EDS analysis of inclusions in tundish samples.

Size (µm)	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	S (%)	CaO (%)	MnO (%)	TiO ₂ (%)
100	-	57.6	27.6	-	2.3	10.8	1.6
1500	5.8	37.3	35.8	-	21.1	-	-
4	2.5	58.1	-	1.1	38.3	-	-
3	2.9	60	-	1.9	35.2	-	-
3	1.9	56.8	-	1.9	39.4	-	-
5	3.1	58.9	-	4.1	33.9	-	-
3	1.7	49.8	-	3.1	45.4	-	-
3	2.8	57.2	-	1.8	38.2	-	-
2	1.6	44.9	-	3.0	50.5	-	-
5	2.9	53.4	-	1.6	42.1	-	-
4	3.1	53.8	-	1.5	41.6	-	-
3	2.1	46.7	-	1.7	49.5	-	-

Table 3: EDS analysis of lining matrix at different depth from the hot surface.

	2 mm	7 mm	10 mm
MgO (%)		7	19
CaO (%)	40	31	35
Al ₂ O ₃ (%)	18	17	
SiO ₂ (%)	36	45	47