CHEMICAL AND STRUCTURAL CHARACTERIZATION OF SLAG COMPOUNDS FORMED IN THE MELTING PROCESSES TO PRODUCE SPHEROIDAL GRAPHITE CAST IRONS

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Abstract

The aim of this research is to investigate the composition and phases present in the slags formed during the production of spheroidal graphite cast irons. This paper contains the results of the first part of such investigation which is focused on those slags generated in the induction furnace, i.e., solid slags formed on the melt surface and slags adhered to quartzite refractory lining. Thus, a group of slag samples of each type were obtained from melts prepared using different metallic charges. These samples were then characterized in order to determine their chemical and structural composition and to evaluate the influence of the raw materials used during melting process on the amount of slag formed in each case. Three different techniques were used for analyzing the slag samples: X-ray fluorescence, X-ray diffraction and scanning electron microscopy with EDS microanalysis. Important differences have been detected among samples studied in this work that have revealed the detrimental role of aluminum on refractory linings. The obtained knowledge has been successfully used to minimize the problems caused by adhesion of slags to refractory linings.

Keywords: spheroidal graphite cast irons, slag compounds, induction furnace, refractory lining, X-ray diffraction, X-ray fluorescence, scanning electron microscopy

Introduction

One of the main problems of spheroidal graphite (SG) cast iron production is the formation of slag compounds that can be formed in any of the various stages of the manufacturing process. The consequence of the formation of these slag compounds depends on the stage in which they are formed. Slag inclusions can be found as an inclusion in the manufactured parts, which is one of the most common defects, but they can also be found, as adhered products in the refractory linings of melting furnaces. In this second case, important reductions on the internal diameter of refractory crucibles are detected which decrease the effective capacity of melting furnaces. In addition to this fact, the formation of such slag accumulations causes cracks and erosion in the silica refractory lining and it promotes failures on the inductor isolation systems. The other important source of active slag is the treatment of base melts with magnesium ferroalloys. These slag compounds have to be properly removed from ladles in order to minimize subsequent contamination problems on pouring devices used in foundry plants. Otherwise such slag products will be rapidly deposited on the refractory lining, and a high risk of degradation will be present in the pouring tools. In general, filters and/or proper filling systems are commonly used in molds for avoiding the appearance of slag inclusions on castings.

In order to avoid the problems related to the formation of slag, it is important to know its chemical composition and those phases present in the slag compound formed at different stages of the production process of SG cast irons. This information becomes useful to determine the affecting chemical elements and which of them are present in the different types of slag commonly found in SG cast iron manufacture. Previous studies on slag formed in spheroidal and lamellar cast irons have shown that it mostly consists of several oxides as FeO, MnO, SiO₂, Al₂O₃ and...
MgO. It has been also reported that these oxides except FeO and MnO are solid in the melting temperature range. According to the Ellingham's diagram, the formation of these oxides is the result of a balance between the oxidation of such elements and the oxidation of carbon for a given temperature. In accordance with the mentioned literature data, there is a temperature range around 1427 °C (2600 °F)–1482 °C (2700 °F) in which slag formation and the appearance of CO gas by carbon oxidation on melts are minimal. These authors observed an increase on slag formation temperature when increasing the silicon content for a given carbon content in the melt. The contrary effect was also detected. It is also reported that re-oxidation reactions occur when free-slag melts cool down, so liquid and solid slag compounds can be formed again due to the oxidation of alloying elements present in the liquid cast iron.

In a more recent work, the influence of metallic charge contents on the amount of slag formed and on its chemical composition was studied though any information about the phases involved was not reported. These authors found the lowest amount of slag after melting when high purity pig iron was used as the main constituent of metallic charges. The worst result (highest amount of slag) was found when using foundry returns composed by shot-blasted ferritic ductile iron casting scrap, while intermediate results were obtained when using steel scrap according to its composition and its source. It was also concluded that the composition of the formed slag depends on the metallic charge type. All metallic charge compositions originated a slag type with similar SiO₂ and Al₂O₃ contents (both were the main oxides) which was obtained from the refractory lining. Slag found when using HPI and steel scrap metallic charges shows relevant amounts of CaO, while MnO was found on slag obtained from metallic charges that mainly contained foundry returns and steel scrap. Finally, slag formed after melting ductile iron returns showed important MgO contents. Surprisingly, any contribution on slag composition of silicon content in alloys and of the raw materials cleanliness (this second parameter mainly affected by external oxidation of pig iron) was not found in that mentioned work.

Katz showed the harmful effects of Fe–O-bearing slag which promote the oxidation of valuable elements such as C and Mn. On the other hand, this slag also sticks on the silica refractory which is the most commonly used in electric furnaces. Additions of SiC in the melting furnace are recommended in this work to avoid this problem. It also reported that such slag sources were sand residues present in the foundry returns and oxidized compounds normally found on raw materials surfaces in case of melting processes made with electric furnaces.

Considering the results of previous studies, two different aims have been approached in this work: the study of the chemical composition changes and of the different compounds found in slag samples depending on the raw materials used for preparing melts and the minimization of detrimental effects caused by slag which is stuck to the refractory linings.

**Experimental Work**

In a first step, six different base melts were prepared in a 6-t capacity medium frequency induction furnace (250 Hz, 4250 kW) using three different metallic charge compositions and two maximum temperatures (see Table 1). In all cases, these raw materials were introduced in the furnace crucible when a remaining amount of melt (around 4000 kg) was present in it. The composition of each remaining melt was the one that corresponds to a standard metallic charge previously melted in the furnace (see Table 2). Note that the FeSi alloy was only used with pig iron and steel scrap-based charges, while graphite and SiC were exclusively used for preparing the melts with steel scrap. After melting and just after achieving the maximum temperature, an alloy sample and a slag sample were simultaneously extracted from each base melt surface. Then, a second sampling was made after skimming the surface of melts and then remaining them in contact with open air for 45 min at each of the two selected maximum temperatures. The first and the second groups of samples will be identified as initial (I) samples and as final (F) samples, respectively. These samples have been also identified according to the metallic charge composition (PI for pig iron, FR for foundry returns and SC for steel scrap) and to the maximum temperature achieved during melting process (00 for 1500 °C (2732 °F) and 45 for 1545 °C (2813 °F), see Table 1). For instance, the P100I code is used to identify the samples that have been initially picked up from the base melt prepared with pig iron at 1500 °C (2732 °F).

In a second step, three slag samples adhered to different refractory linings of the induction furnace have been studied. These samples were removed from the refractory surface at the end of the life span of the furnace linings which duration was not systematically the expected one due to failures on the inductor isolation system. In these cases, the metallic charge composition was commonly used in the manufacturing process of the foundry plant (Table 2) and the melting procedure was similar to the one detailed above. These samples will be identified in the text as UC11, UC31 and UC32 where UC notation refers to “usual charges,” the first number is the furnace identification and the second one is the sample number.

In a third step of the present work, a set of experiments were made in order to obtain more information about the formation of slags stuck to the refractory linings. Thus, two different metallic charges, one based on foundry returns and the other one based on steel scrap, were exclusively...
used for preparing all the base melt batches during the whole life span of each refractory lining in the furnace. Table 2 shows the composition of these two metallic charges which were introduced in the furnace with around 4000 kg of remaining melt except in the first charge where the furnace was empty. In all cases, the maximum temperature achieved during the melting process was 1500 °C (2732 °F). After finishing the life span of these two refractory linings, a slag sample was obtained from each one for later characterization. These two slag samples are identified as FR21 and SC31 where FR and SC notations refer to foundry returns or to the steel scrap-based charges, respectively. The first number is the furnace identification, and the second one is the sample number.

Chemical compositions of melts were determined on samples picked up from the prepared alloys during slag sampling. These analyses were performed using a combustion technique (LECO CS200) for carbon and sulfur and spark emission spectroscopy (ARL Metal Analyzer Iron + Steel) for the rest of elements. X-ray fluorescence (XRF), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) and EDS microanalysis were used to characterize the constituent phases formed on each slag sample by means of a PANalytical X’Pert PRO MPD q/q Bragg–Brentano powder diffractometer 240 mm (9.45 inches) in radius. The slag samples were crushed in an agate mortar until micrometer size. Then, the sample was placed in a rectangular standard holder 20 mm (0.79 inches) in length, 15 mm (0.59 inches) in width and 1 mm (0.04 inches) in height in order to obtain a flat surface by manual pressing of the powder material using a glass plate.

Scanning electron microscopy and EDS microanalysis (SEM–EDS) were used to corroborate the results obtained from the two other techniques and to check the slag samples’ microstructure. For this purpose, the raw samples were broken in small pieces and then were embedded in

### Table 1. Temperatures of Melts Prepared in the Induction Furnace and Metallic Charge Compositions (kg)

| Sample      | Pig iron | Steel scrap | Returns | Graphitea | FeSiab | SiCc  |
|-------------|----------|-------------|---------|-----------|--------|-------|
| PI00/PI00F  | 1500 (2732) | 1923        | –       | –         | –      | 31    |
| FR00/FR00F  | 1500 (2732) | –           | –       | 1838      | –      | –     |
| SC00/SC00F  | 1500 (2732) | –           | 1866    | –         | 75     | 29    |
| PI45/PI45F  | 1545 (2813) | 1966        | –       | –         | –      | 41    |
| FR45/FR45F  | 1545 (2813) | –           | 1890    | –         | –      | –     |
| SC45/SC45F  | 1545 (2813) | –           | 1838    | 67        | 24     | 19    |

a Carbon content: 99.9 wt%
b FeSi composition: 75.2 wt% Si, 0.7 wt% Al and 0.3 wt% Ca
c SiC composition: 65 wt% Si, 25 wt% C and 0.8 wt% Al

### Table 2. Metallic Charge Compositions Used in the Induction Furnace (wt%)

| Sample     | Pig iron | Steel scrap | Returns | Graphitea | FeSiab | SiCc |
|------------|----------|-------------|---------|-----------|--------|------|
| FR21       | 2.6      | 30          | 65      | 1.2       | 0.2    | 0.5  |
| SC31       | 3.0      | 65          | 28      | 2.6       | 1.0    | 0.7  |
| Usual charge (UC) | 2.5 | 37          | 59      | 1.4       | –      | 1.0  |

a Carbon content: 99.9 wt%
b FeSi composition: 75.2 wt% Si, 0.7 wt% Al and 0.3 wt% Ca
c SiC composition: 65 wt% Si, 25 wt% C and 0.8 wt% Al
Results and Discussion

Slags Generated in Induction Furnaces

After melting the metallic charge and then stopping the induction power in the furnace, the slag formed is normally found as scabs which are floating in the melt surface. These slags are formed in the melt surface areas that are close to the refractory lining, but then they become aggregated in a crust form found in the central area. Once extracted from the melt and then cooled at room temperature, the slag shows an apparent vitreous morphology and a dark gray color. A second inspection of melts surfaces after skimming process shows that more slags were gradually formed in the surface of melts. Color and morphology of these recent slag compounds are similar to the ones initially obtained. The chemical composition ranges of the prepared melts are shown in Table 3. It is noted that the alloy obtained when using the steel scrap-based charge shows aluminum, manganese and zinc contents that are significantly higher than the two others. On the other hand, aluminum has been also added by means of SiC and FeSi products that were used for adjusting the melt composition in these cases (Table 1). However, the last product does not seem to be very relevant in this sense as aluminum contents are higher for alloys prepared with charges based on returns than for those prepared using pig iron as main raw material (Table 3). On the other hand, the use of returns seems to be the cause of the highest silicon contents observed on the base alloys investigated. The highest sulfur levels are found when using pig iron-based charges due to the high content of this element commonly found in this raw material.

The results obtained from the XRF analyses performed on the twelve slag samples collected from base irons can be seen in Table 4. In this table, only those values higher than 1.00 wt% are shown. The results indicate that silicon oxide is the main constituent of all these samples. Thus, SiO₂ is shown to be the most important oxidation product in melts as silicon is the main alloying element and this element exhibits a high tendency to be oxidized. As can be expected, the four slag samples obtained from the melt prepared using foundry returns show the highest SiO₂ contents (Table 4) due to the sand adhered to these raw materials and owing to the high silicon content found on the corresponding base melts (see Table 3). The SiO₂ content is also higher in the slag samples extracted after 45 min than in those collected just after melting. This result could be related to the progressive oxidation of silicon while keeping melts in the furnace at a given temperature. However, a similar effect due to the use of high temperatures has not been detected.

The aluminum oxide content in the slag samples obtained from the two steel scrap-based melts is higher than the ones extracted from the pig iron-based melts. Although the exclusive SiC addition made when preparing the steel scrap-based melt can be related to this fact, another important available source of aluminum can be the own steel scrap. The Al₂O₃ content is also higher in the samples obtained from melts that were remaining in the furnace than the ones obtained just after melting the metallic charges. This is probably due to the progressive oxidation of aluminum present in the liquid alloy during the remaining time. The high CaO levels found in the slag samples collected from the melts prepared using steel scraps and pig iron can be explained by the addition of the FeSi ferroalloy. Clear tendencies when comparing the chemical compositions of the slag samples obtained at 1500 °C (2732 °F) or at 1545 °C (2813 °F) are not observed.

The XRD analyses carried out on all the slag samples studied in the present work support the results obtained by XRF. Floating slags generated in the induction furnace are mainly composed by amorphous phases. The two main phases with crystalline structures that have been found on these samples are quartz and cristobalite (SiO₂). Quartz is the stable phase at temperatures lower than 867 °C.

Table 3. Chemical Compositions of the Base Melts Prepared in the Present Work (wt%)

| Samples   | C   | Mn | Si  | S   | Mg  | Al  | Ti  | Ce  | Zn  |
|-----------|-----|----|-----|-----|-----|-----|-----|-----|-----|
| PI00/PI00F| 3.90| 0.18|2.02 |0.020|0.002|0.024|0.0018|0.079|
| FR00/FR00F| 3.83|0.22 |2.12 |0.011|0.003|0.023|0.0019|0.081|
| SC00/SC00F| 3.79|0.29 |1.97 |0.014|0.002|0.021|0.0024|0.199|
| PI45/PI45F| 3.98|0.18 |1.78 |0.021|0.002|0.021|0.0021|0.091|
| FR45/FR45F| 3.85|0.20 |1.98 |0.014|0.003|0.024|0.0024|0.107|
| SC45/SC45F| 3.76|0.21 |1.82 |0.014|0.003|0.0066|0.031|0.0023|0.218|

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In addition to the main SiO₂ phases, minor amounts of some silicates and other oxides have been also detected in five of the slag samples analyzed by XRD. Magnesium silicates are found in two of the slag samples obtained from base melts prepared with foundry returns (FR00I and FR45F). In the sample FR45F, a magnesium iron oxide (MgFe₂O₄) is also found. The presence of these Mg-bearing slag compounds in such samples is related to the use of ductile iron returns as raw materials when preparing the base melts mentioned above. On the other hand, crystalline iron silicate (Fe₆SiO₁₁Cl₂) and iron oxide (Fe₂O₃) are, respectively, detected on PI00I and PI45F samples, while zinc silicate (Zn₂SiO₄) is present in the SC45F sample. In this last, zinc oxide (ZnO) and an aluminum zinc oxide (ZnAl₂O₄) are found too. As expected, the iron silicate is found in a sample obtained from a melt prepared with pig iron (surface oxidation), while the zinc compounds are only detected when galvanized steel scrap is used as raw material during melting. Figure 2 shows the XRD spectrum and indexation of the three crystalline phases found in the FR00I slag sample, i.e., quartz, cristobalite and pigeonite (Mg,Ca,Fe)SiO₃. On the other hand, Figure 3 illustrates the crystalline growth of a silicate-type compound (a) found in the same sample and the results obtained from the SEM–EDS microanalysis (b) of such compound.

Besides, some nondissolved particles of SiC and/or FeSi were detected by XRD on samples obtained from melts prepared using these additives (see Table 1). Subsequent SEM analyses made on such samples confirmed these results. As it has been stated before, the zinc content both in the prepared melts and in the slag samples extracted after melting becomes high when the steel scrap-based metallic charges are used as the galvanized steel scrap from the automotive industry is the main constituent of these charges. This fact is confirmed by means of the XRD analysis made on the slag samples. Figure 4 shows the XRD diffractogram recorded on the SC45F slag sample where the minor crystalline phases are very easily identifiable even though a high content of amorphous phases is found in this sample. Thus, peaks of Zn₂SiO₄ (willemitite) and ZnO are detected in addition to the ones that belong to ZnAl₂O₄ (gahnite), the latter only appearing in this slag sample. Although all these zinc-bearing phases have not been detected by SEM analysis because they are present in a very minor amount, the microanalysis made on the amorphous phase of the SC45F slag sample shows a small peak of zinc (this sample contains the highest ZnO and Al₂O₃ contents of all samples analyzed) (see Table 4).

### Slags Adhered to the Refractory Lining of Induction Furnaces

**Characterization of Slags (Standard Metallic Charges)**

After emptying and then cooling, the furnace crucible slags adhered to the refractory lining are detected in an area located close to the bottom of the crucible and at 1/3 of its height. These slags are typically composed of a mixture of different phases, including iron silicate, silicon oxide, and zinc oxide. The chemical composition of these slags can vary significantly depending on the specific conditions of the melting process. The presence of these phases is important for the performance and durability of the refractory lining, as they can affect the thermal shock resistance and abrasion resistance of the lining material.
total height. This affected area always remains in contact with the liquid alloy even after tapping the furnace according to the usual procedure of the plant. The thickness of the slags found in this affected area ranges from 20 mm (0.79 inches) to 150 mm (5.91 inches), and they seem to be heavier than those floating slags directly obtained from melts. Figure 5 shows a general view of a discharged refractory lining of a furnace. The zone marked as 1 in this figure is the worn part of the refractory lining. Notice that the expected thickness of the used refractory lining can be found in the upper levels (marked in Figure 5 with arrows). The adhered slags were found below zone 1, and they affect the whole section of the lining at this lower level (zone 2 in Figure 5).

Quartzite refractory areas in contact with slag showed a darker region with around 1 cm in thickness which is marked by arrows in Figure 6a. A general view of a slag...
that was stuck to the refractory lining is shown in Figure 6b. Regarding the refractory material, both a free-slag region and a darker region of a sample were analyzed by SEM–EDS. Only the expected peaks of silicon and oxygen were found for the free-slag region. However, detailed examinations on the darker region revealed the existence of slag penetrations similar to “veins” (indicated by arrows in Figure 7a) where extra peaks of aluminum, magnesium, calcium and cerium were detected in addition to the peaks of silicon and oxygen (see Figure 7c). Most of these further elements found in the darker region are in good agreement with the use of standard metallic charges where returns become the main constituent (Table 2). Here it is worthy to emphasize the relevant intensity of the aluminum peak even though this element does not seem to be the most expectable one.
according to the composition of the standard charges used here. In Figure 7b, a detailed view of a slag vein is also shown which is surrounded by SiO₂ grains. These slag penetrations in the refractory areas in contact with adhered slag probably make them darker.

Table 5 shows the chemical composition of the three slag samples that were collected from the discharged refractory linings. In this table, only the oxides with content higher than 1.00 wt% were included. Surprisingly, all three samples are mainly composed by Al₂O₃ and MgO, while SiO₂ becomes now a minority oxide when comparing to data include in Table 2. MgO and Al₂O₃ are two of the oxides included in Table 5 with the highest melting point, i.e., >2000 °C (3632 °F), so they should be more prone to be stuck to the refractory material than the rest of possible oxides. On the other hand, quartzite, i.e., the refractory material used in the present work, is essentially composed by SiO₂ which is considered as an acid oxide. Thus, one can expect that the basicity and the amphoteric characteristics of MgO and Al₂O₃, respectively, also become a relevant cause of the reaction between these slags and the refractory material.

The available source of magnesium seems to be the foundry returns used as raw materials; however, the sources of aluminum are numerous. In this second case, possible supplies are the use of additives as ferrosilicon, silicon carbide, the use of steel scraps and also of foundry returns as raw materials. According to this fact and to the high Al₂O₃ content found in all the slag samples obtained from the refractory linings, it could be considered that aluminum plays a very relevant role on refractory degradations in electric furnaces and consequently on the life span reduction in these devices. Table 5 also shows important amounts of cerium oxide and lanthanum oxide in these slag samples in comparison with those samples obtained directly from melts. The presence of these two elements should be related to the massive use of foundry returns as raw materials in the melting furnace. Notice that these returns are manufactured with the use of FeSiMg and of inoculants which both contain rare earth elements.

Another main phase (marked as 2) is composed by a group of elements (calcium, cerium, lanthanum, silicon, sulfu...
and oxygen) which can form complex sulfides and oxides. Finally, peaks of calcium and sulfur (likely to form CaS) are present in phase 4 which grew as isolated particles in phase 3, this latter composed by magnesium, silicon, calcium and oxygen.

The XRD diffractogram shown in Figure 9 was obtained from the UC32 slag sample. It can be seen that it contains a much smaller amount of amorphous phases than the slag samples obtained from the melts surface (see Figure 4). The UC11 and UC31 samples exhibit a similar behavior.

This high crystalline degree must be related to the observed heavy aspect of these slags when comparing to the floating ones.

The most important crystalline phase found in the UC32 sample is the MgAl₂O₄ (spinel) which is formed by reaction between the two main oxides MgO and Al₂O₃ present in these slags (Table 5). This result confirms the relevant role of aluminum previously predicted in the SEM inspections carried out on the slag-affected regions of refractory (Figure 7). On the other hand, this phase has been also detected in the SEM analysis of the UC11 slag sample shown in Figure 8 (phase 1). The crystalline

**Figure 7.** SEM micrographs of the refractory lining: Showing the slag (light zone) veins by arrows adhered to the darker region (refractory lining) (a); detail of the affected zone of the refractory (b); below the SEM–EDS spectrum of this affected zone is shown (c).

**Table 5.** Chemical Composition of Slags Stuck to the Refractory Lining Analyzed by XRF (wt%)

| Sample | Al₂O₃   | MgO   | SiO₂   | CeO₂  | Fe₂O₃  | CaO   | La₂O₃  | SO₃  |
|--------|---------|-------|--------|-------|--------|-------|--------|------|
| UC11   | 43.45   | 27.67 | 10.71  | 6.19  | 2.89   | 3.30  | 2.47   | 1.69 |
| UC31   | 61.81   | 24.95 | 5.86   | 2.87  | 1.72   | 1.37  | –      | –    |
| UC32   | 37.59   | 39.96 | 4.68   | 6.58  | 2.63   | 3.72  | 2.63   | 1.28 |

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phase MgO (periclase) is also detected in the XRD index- 
ation shown in Figure 9. This fact indicates that an excess of MgO which has not reacted with the Al$_2$O$_3$ to form the spinel is present in the UC32 sample. In fact, this sample showed the highest MgO content (Table 5). Other minor phases identified in Figure 9 are CaMgSiO$_4$ (monticellite) and SiO$_2$ (quartz). The former compound has been also detected in Figure 8 for the UC11 sample (phase 3).

Figure 8. SEM micrograph of the UC11 slag sample (top). Below the EDS microanalysis spectra of the phases marked on micrograph are shown.
Comparing to the results obtained for the UC32 sample, the XRD characterization of UC11 and UC31 samples also showed a high crystalline degree. MgAl₂O₄ (spinel) was detected as the main crystalline phase and CaMgSiO₄ (monticellite) and (Mg,Fe)₂SiO₄ (forsterite) were identified as minor phases. It is worth noting that CaMgSiO₄ and CaS compounds had been already detected as phase 3 and phase 4, respectively, in the SEM-ESD analysis performed on the UC11 sample (Figure 8). The (Mg,Fe)₂SiO₄ (forsterite) compound which is formed by the reaction between MgO and SiO₂ is only present in the UC11 slag sample as is shown the highest SiO₂ content (Table 5).

Origin of Slags Adhered to Refractory Linings

Once identified the spinel phase MgAl₂O₄ as the main constituent of slags adhered to refractory materials, it is now worthy to investigate the origin of this phase and some of its influencing factors. As it has been described in the experimental section, two different metallic charge compositions (mainly composed by foundry returns or by steel scrap) were separately used during the whole life span of each refractory lining of the furnace following a similar melting procedure. Malfunctions owing to the presence of slag stuck to the refractory lining were detected after 214 melting batches when steel scrap-based charges were only used in the melting furnace. However, no failure occurred after 724 melting batches when exclusively using the return-based charges.

Another important difference is the amount of slags adhered to the refractory linings at the end of their life span. The lining where only steel scrap-based charges were used for melting shows massive slags stuck to the entire refractory ring located in the usual region described above. However, only specific zones of the lining were found to be affected when return-based charges were exclusively used following a similar melting procedure. Thus, it can be concluded that slag formation was more "aggressive" in the first case, based on the use of steel scrap-based charges.

XRF chemical compositions of the two slag samples collected from the linings are shown in Table 6 where only those contents higher than 1.00 wt% are included. It can be seen that the MgO, CeO₂ and La₂O₃ contents are higher for the sample obtained from the return-based charges than for the one coming from the steel scrap-based charges. On the contrary, the Al₂O₃ content is much lower in the FR21 sample than in the SC31 sample. These results are expected as foundry returns become a notorious source of the three elements previously mentioned (they were manufactured using a FeSiMg alloy and inoculant), while steel scrap and the adjusting products (SiC and FeSi) contain significant amounts of aluminum. These auxiliary products should also be considered as the source of Ca and Zn in case of the slag sample formed in steel scrap-based melts.

Regarding the phases identified by XRD for these two slag samples, the spinel MgAl₂O₄ is the most abundant crystalline phase on the FR21 sample (see the diffractogram shown in Figure 10 below). Additionally, an important amount of MgO (periclase) has been also found in this sample. The crystalline phases detected on the SC31
Table 6. Slag Samples Composition Analyzed by XRF (wt%)

| Sample | Al₂O₃ | MgO  | SiO₂ | CeO₂ | Fe₂O₃ | CaO  | La₂O₃ | SO₃ | ZnO |
|--------|-------|------|------|------|-------|------|-------|-----|-----|
| FR21   | 30.17 | 36.56| 8.69 | 9.29 | 2.79  | 4.29 | 3.78  | 2.15| –   |
| SC31   | 60.61 | 7.48 | 16.66| 1.16 | 4.60  | 6.28 | –     | 1.13| 1.13|

Figure 10. XRD diffractogram and indexation of: the SC31 sample (above) and the FR21 sample (below).

Figure 11. Schema of the steps proposed for the adhered slags formation in the quartzite refractory linings.
sample are quite different (Figure 10 above). In this case, many phases that contain aluminum and calcium have been found, being the most relevant the MgAl₂O₄ spinel, Al₂O₃ (corundum), CaAl₂Si₂O₈ (anorthite) and an aluminum–calcium oxide known as hibonite. These XRD outcomes are in good agreement with the differences shown in Table 6, all confirming the negative effect of aluminum on life span of refractory linings.

A scheme that illustrates the mechanism and the probable reactions involved in the formation of slags adhered to the refractory linings is shown in Figure 11. Part of the aluminum dissolved in the melt would react with the quartzite giving aluminum oxide and silicon as final products. Similarly, the magnesium dissolved can react with the refractory material to obtain magnesium oxide and silicon. Thus, these two oxides would be present close to the lining, so they can react to form the spinel (MgAl₂O₄) previously characterized as the main phase of these detrimental slag compounds.

Additional experiments were made using different melting furnaces in order to evaluate the detrimental effect of aluminum coming from FeSi and SiC products. Thus, apparently favorable metallic charges composed 58% foundry returns, 37% steel scrap, 2.5% pig iron, 1.7% graphite and 0.8% FeSi with a low aluminum content (0.029 wt%) and without any SiC addition were exclusively used during the whole life span of 22 refractory linings. As a result of these experiments, it was observed that slags were adhered to 20 discharged refractory linings, whereas they were not found in the other 2 ones. When SiC was reintroduced again to metallic charges according to the standard composition of charges (Table 2), both the percentage of affected linings and the amount of slags adhered to them slightly increased. These results show the important role of steel scrap as the main aluminum source of melts prepared in the present work.

**Conclusions**

Characterization of the slag samples analyzed in the present work has led to know both the chemical and structural differences between slags formed in the upper surface of melts and those adhered to the refractory lining of medium frequency induction furnaces. In this second case, serious malfunctions are normally detected on these devices which force to stop the melting process and finally to replace the refractory lining with important extra costs for foundry plants. The main conclusions of this work are the following:

1. Slags floating in melt surfaces contain high amounts of amorphous constituents probably due to their rapid formation. This fact could explain the vitreous aspect normally found on these slags at room temperature. The majority crystalline phases detected on these floating slags are SiO₂ as quartz and cristobalite. The rest of compounds (oxides) detected by XRF and not identifiable by XRD techniques are included in the amorphous fraction of this slags.

2. In general, significant differences have not been detected regarding chemical composition and constituent phases between the slag samples collected just after finishing the melting of metallic charges and the corresponding ones obtained after remaining melts in contact with open air for 45 min. In this sense, only an increase in some oxides as Al₂O₃ was found in case of samples from steel scrap-based charges.

3. Floating slags formed when using steel scrap-based charges showed the highest zinc and aluminum contents and they are the only samples where a crystalline phase (ZnAl₂O₄, gahnite) different than SiO₂ was detected by XRD techniques. These high zinc and aluminum contents are due to the use of galvanized steel scrap as raw material (Zn and potentially Al) and of FeSi and SiC as additives (Al). On the other hand, rests of nondissolved additives as FeSi, SiC and graphite have been also detected on these samples.

4. In case of slags formed from return-based charges, zinc and aluminum contents are low, while the content of those elements involved in the manufacture of ductile iron castings (Mg, Ce and La) becomes comparatively high. The XRD analyses made on these slags revealed the existence of minor amounts of silicates that contain these specific elements in addition to the SiO₂ phase.

5. Slags attached to the quartzite refractory lining of the induction furnaces and considered as the more detrimental ones mainly consist of MgAl₂O₄ (spinel) which is probably formed by reaction between Al₂O₃ and MgO compounds.

6. Slags adhered to the refractory lining show chemical compositions quite different from those found in floating ones. In the former case, Al₂O₃ and MgO become the most abundant oxides on the samples analyzed and their content depends on the metallic charge composition and on the amount and type of additives used during the melting procedure. It has been demonstrated in the present study that the highest amount of slags stuck to the refractory material were found when a high content of Al₂O₃ is present in the slag composition. Thus, aluminum must play a critical role in the detrimental effect of these slags on the life span of refractory linings.

7. It has been checked that those adhered slags with a high Al₂O₃ content and considered more "aggressive" against quartzite linings are promoted when using steel scrap-based metallic charges during melting. This result leads to think that steel scrap...
is the most important available source of aluminum though SiC and FeSi products have also to be taken into account regarding this sense. Finally, it has been possible to minimize the formation of slags adhered to linings by reducing the aluminum sources in raw materials and additives used in the melting processes. An effective control to keep a proper balance among MgO, SiO₂ and Al₂O₃ oxides during melting should be quite helpful to prevent the formation of the MgAl₂O₄ spinel phase and consequently of these harmful slags.

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