Evaluation of Interactions between Refractory Materials and Steel Melt by using a Steel Casting Simulator

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ABSTRACT

For investigations of interactions between refractories and steel melt, a so called steel casting simulator located at the institute of Ceramic, Glass and Construction Materials in Freiberg (Germany) is used. Different experimental setup can be applied to investigate the interactions between refractory components and steel melts with different compositions. Porous filters or dense prismatic materials can be dipped and rotated in steel melt which contains a defined amount of endogenous inclusions. In case of this setup it's possible to remove and cool down the test materials under oxygen free conditions to exclude overlaying atmospheric reactions, e.g. carbon oxidation in case of carbon containing materials. These experimental set-ups enable the investigation of filter materials with different surface chemistry and attached non-metallic inclusions after steel melt contact. Crucible tests are performed under the same conditions with various steel melts under the aspect of long-term stability of new developed materials under reproducible conditions. The simulation of metal casting through model nozzles allows the investigation of clogging phenomena simultaneously at two model samples for each trial.

KEYWORDS

Testing Device; Refractories; Steel

INDRODUCTION

The interaction of refractories with steel melt as well as non-metallic inclusion in the melts is of great importance for steel producing as well as for refractory industries.
Non-metallic inclusions can decrease dramatically the properties of steel products depending on the size, type and distribution. These inclusions are mainly oxides, carbides, nitrides and sulphides [1]. They can be divided after their origin into endogenous (deoxidation products, precipitation during cooling and solidification) and exogenous inclusions (slag entrainment, lining erosion). To remove inclusions ceramic filters with various macro-structures are successfully applied since several decades. [2]
To understand the kinetic of the interactions between non-metallic inclusion and filter surface, especially the surface chemistry, is important to develop new filter structures and materials with increased filtration efficiency. The interaction of steel melt with refractory materials is also of great interest in case of steel cleanliness as well as refractory performance. Therefore a unique test system, a so called steel casting simulator was developed. Steel melt filtration experiments in form of immersion tests as well as casting tests through real filter geometries were performed under fully controlled conditions. Flow melt experiments through model nozzles were performed additionally to investigate the interactions of refractory surface and non-metallic inclusions containing steel melt.

EXPERIMENTAL PROCEDURE

Immersion tests (finger tests), crucible tests as well as casting tests through model-nozzles were done in the steel-casting simulator. The principle setting is presented in Fig. 1.
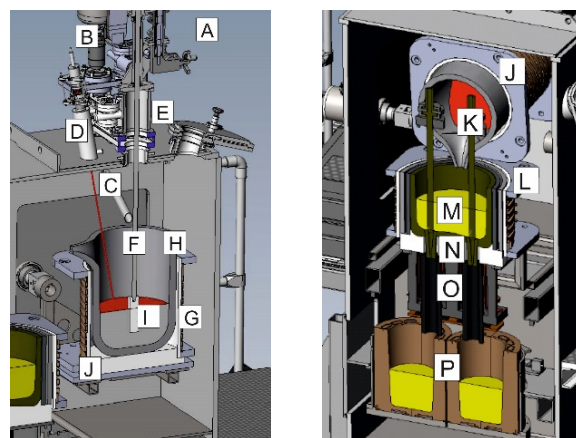

Fig.1. Steel casting simulator - Melting unit with revolver system used for finger tests (left) and tundish unit (right)

The system is composed of a two separated inductive-heated units, the melting unit (150 kVA) and the tundish unit (100 kVA), inside a gas tight water-cooled housing. In top of the melting unit a revolver system is placed. This rotatable system consists of an oxygen/temperature measuring system (A), a sampling system (B) and a finger-test system (E) for immersion of prismatic samples in steel melt. A dosing unit (C) is also situated above the melting unit to add alloying elements or slag-forming agents. The alumina-based melting crucible (H) is placed inside the induction coil (G). The melting unit can be inclined (J) to fill the melt into the tundish unit (L). This unit consists of a carbon crucible which acts as a heating unit. Inside that an oxide crucible (alumina/mullite based castable) is fitted in to prevent carbon pic-up of the test-melt. Three nozzles (N) are placed in the basement (two for tests and one for security reason) and a stopper rod system (K) to control the melt flow through the nozzles, the two test zones (O) into the water cooled copper moulds. Weight cells are placed under the tundish as well

under the two moulds to register the weight chance during casting for the calculation of flow rates.

For the casting tests model nozzle's (120 mm length, inner diameter 5 mm, wall thickness 5 mm) based of alumina and carbon were produced by slip-casting in plaster moulds, dried at 120 °C and fired in coke-grid at 800 °C. For an additional coating a second slurry (alumina, carbon-free) were produced and an additional slip-casting step was used with the porous fired nozzle instead of the mould to coat directly the inner surface. A second drying and firing step at 1400 °C under coke-grid subsequently followed. [3]

For the test commercial available steel 42CrMo4 (Mat. No 1.7225, AISI 4142) in cylindrical shape ingots are placed in the melting crucible and heated up to 1650 °C in 90 min under Ar atmosphere. The oxygen content as well as the temperature of the steel-melt was measured with an oxygen/temperature sensor-system A (Heraeus Multi-LabIII CELOX). After melting, the steel-melt is poured into the tundish unit, which is in advance preheated to prevent major heat loss of the melt. A short time after pouring the melt (30 sec) into the tundish, the stoppers rods are lifted simultaneously and the melt flows through the two test nozzles into the cooled copper moulds. The configuration of the nozzle test zone is shown in Figure 2.
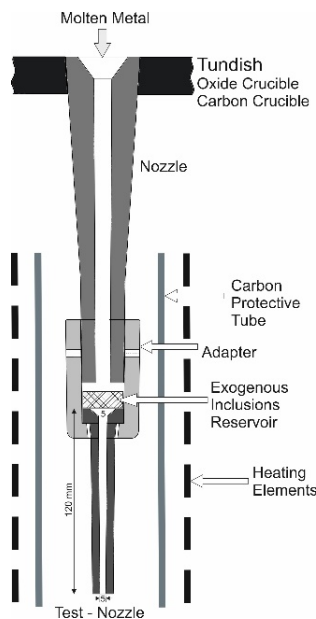

Fig. 2. Configuration of the testing nozzle area

With the aid of an oxide based adaptor system (Fig.2), a carbon bonded test nozzle is inserted in the adaptor and fixed above the water cooled copper mold. Inside the adaptor a so called exogenous inclusions reservoir is placed above the test nozzle to add defined impurities to the flowing steel. This reservoir consists of a carbon-bonded alumina 10 ppi filter (diameter 30 mm, thickness 20 mm) and an unsintered coating of impurities. The coating consists of a mixture of artificial impurities of equal amounts of alumina and spinel, both with a maximum grain size of 100 μm. The test zone with the test nozzles is preheated by CFC-heating elements up to 1600 °C to prevent freezing of the liquid metal and to adjust a constant testing temperature in the nozzle area. The

masses of the tundish unit and the two copper moulds are recorded during the experiment by load cells. After each test the nozzles were investigated by SEM and computer tomography.

For immersion tests, especially for the evaluation of the filtration efficiency of filter materials prismatic 10 ppi filter samples (125 x 20 x 20 mm³) were fixed at the sample holder (F) and were entered into the simulator through a sewer port. After immersion with rotation (30 rpm) the sample cooled down nearly steel-free under argon atmosphere. The steel for this kind of test was molten in a secondary crucible which was placed inside the melting crucible (H). This crucible based on alumina-spinel alkali- and calcia-free refractory castable to minimize the interactions of the steel-melt and the crucible. For each immersion test approx. 30 kg of steel blocks are placed inside and were melted under Ar-atmosphere. The temperature and the content of dissolved oxygen in the molten steel were measured with a po2/T sensor system (A) during heating and before and after the immersion of the tested filter sample in each individual melt, with new crucibles each time. After the immersion with an additional rotation of 30 rpm the sample was removed and cooled down nearly steel-free under Ar inside the chamber (E).

The alumina-carbon based filter materials with additional functional alumina-coatings were produced using the replica process and additional spray coating step as presented in detail in Emmel [4].

To create defined alumina impurities in situ in the steel melt, especially for the immersion tests, 0.5 wt.-% of a defined iron oxide mixture were added. The commercially available product (Mineralmühle Leun, Germany) consisted of 75 wt.-% hematite and 25 wt.-% magnetite. After setting a temperature of 1650 °C, the oxide mixture was added directly to the melt and an increase of the dissolved oxygen from approx. 10 ppm up to approx. 60 ppm was measured. To create the required endogenous alumina inclusions, 0.05 wt.-% of pure aluminum metal was added to the melt. Due to this deoxidizing step, the dissolved oxygen content of the melt was decreased to the starting values. Through the reaction between oxygen and aluminum, finely dispersed aluminum oxide was formed. [6]

RESULTS AND DISCUSSION

CASTING TESTS

The down end of an alumina coated (left) and uncoated alumina-carbon nozzle (right) is presented in Fig. 3. The comparison shows a significant visible difference between both inner parts.
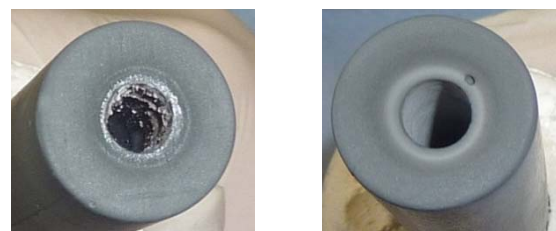

Fig. 3. Lower ends of alumina coated (left) and uncoated alumina-carbon nozzle after casting test at 1600 °C

The comparison of the recorded mass versus time curves is shown in Fig. 4. After a similar behaviour till 150 s a significant difference between the coated and uncoated nozzle is visible. Both had a starting inner diameter of 5 mm.
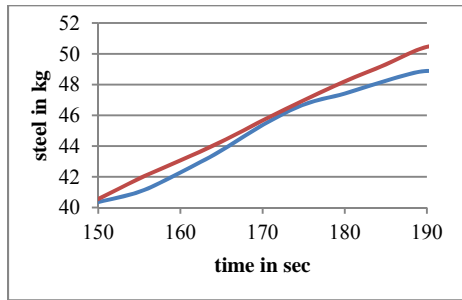

Fig. 4. Steel mass versus process time of uncoated (blue) and alumina coated (red) model nozzles

Foregoing research work of alumina coated alumina-carbon nozzles show differences in the clogging behavior of endogenous as well as exogenous non-metallic particles on alumina-coated and uncoated nozzles during simultaneous tests in the described steel casting simulator [3]. In Fig. 5 the clogging layer inside the alumina coated nozzle after steel contact is presented. This layer consists of two areas, a dense zone (II) in the range of 35 µm and coral-like zone (I) in the range of 60-80 µm. A similar, less dense and with lower thickness layer build-up was also detectable in case of the uncoated material.[3] [4]
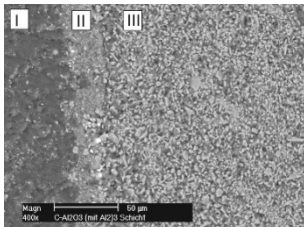

Fig. 5. Loose clogging layer (I), dense layer (II) on alumina coating after casting of steel at 1600 °C

The comparison of the CT-results between alumina-coating and the uncoated reference are presented in Fig. 6. In the lower inner part some white particles (steel drops) and few smaller grey particle (clogged inclusions) are visible in case of the alumina coated nozzle.
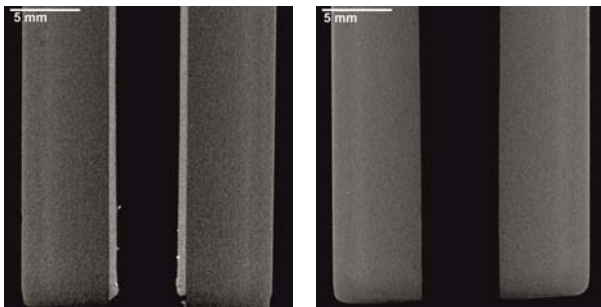

Fig. 6. CT-Images of the down parts of alumina coated and uncoated alumina-carbon nozzles after casting at 1600 °C, 23 µm voxel resolution

IMMERSION TESTS

A wide range of different coatings on alumina-carbon based filter material are tested. The base-material alumina-carbon as well as two interesting coatings, alumina and magnesia-carbon will be presented hereinafter. In Fig. 7 a sample before and after dipping for 30 s is presented
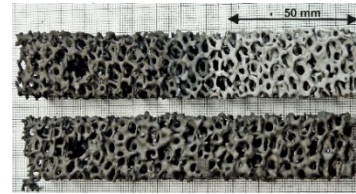

Fig. 7. Prismatic filter samples before (below) and after immersion test (above)

The dipping of magnesia-carbon coated samples leads to degrease of the solved oxygen in the steel melt. Immersion of 30 s into 30 kg steel reduces the oxygen content from 30 to 27 ppm at each trial. The investigation of the greyish coloured zone, the contact zone, is shown in Fig. 8.
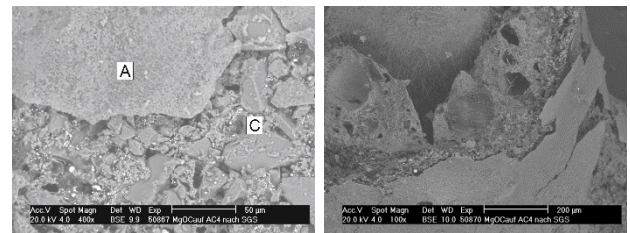

Fig. 8. MgO-C coated Al_2O_3-C filter material after 30 s steel contact

After steel contact a new formed secondary magnesia layer on the surface (A in Fig. 8) as well as secondary magnesia particles on this secondary layer were be detect by SEM/EDX and identified with the aid of EBSD as MgO. Inside the hollow struts secondary Al-Mg-spinel whisker were identified. These facts show the evidence of carbothermal reduction of magnesia as well as alumina at a test temperature of 1600 °C in presence of iron melt which contributes catalytically. [5] [6]

The immersions of the alumina-carbon base-material at the same conditions show similar results. A new formed secondary alumina-layer with deposited alumina-based particles could be found on the alumina-carbon based material (Fig. 9) as well as with additional in situ formed alumina coating (Fig. 10). [6]
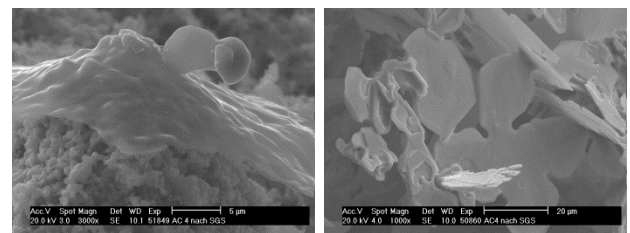

Fig. 9. Alumina-carbon base-material after immersion in steel melt, secondary in situ formed alumina-layer (left) and deposited alumina inclusion from the melt

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The carbon bonded alumina sample coated in advance with a pure alumina coating on the top is presented in Fig. 10. With the aid of EBSD a secondary α-alumina-layer (layer E in Fig.10) was detected at room temperature with a thickness between 150 and 400 nm. This in situ formed layer follows the roughness of the porous primary alumina coating (layer D) on the top of the alumina-carbon base-material. Just below this layer D an additional carbon free layer C can be detected. The carbon of this area/layer was consumed for the carbothermal reduction of the alumina of the filter. [6]
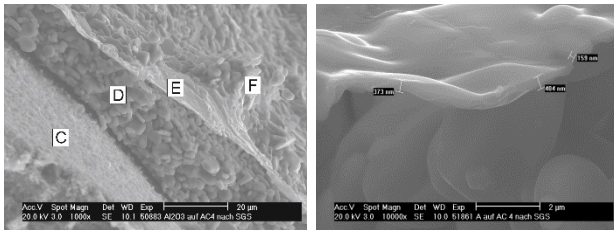

Fig. 10. Alumina-coated alumina-carbon based material after immersion in steel melt, layer composition (left) secondary alumina layer in detail (right)

CONCLUSIONS

Carbon bonded alumina nozzles with and without additional functional coatings have been tested simultaneously in the steel casting simulator according to their clogging performance against non-metallic inclusions. A "denser" and a "coral-like" clogging layer have been identified in both cases, whereby a thicker layer has been registered in case of the alumina-coating. The higher clogging tendency of the alumina-coating leads to a decrease of the steel-melt flow in comparison to the uncoated material, due to the clogging-layer build-up. In means of filtration it can be assumed that the alumina coating contributes to higher filtration efficiency.

The immersion of magnesia-carbon coated Filter materials had shown that a secondary magnesia layer had been formed due to the carbothermal reduction of magnesia and reoxidation of the gaseous magnesium at the contact zone between refractory material and oxygen containing steel-melt. Inside the hollow filter struts spinel whiskers had been registered. The presence of the spinel components magnesia and alumina insight the alumina-carbon material indicates the carbothermal reduction of magnesia and additionally alumina in presence of iron. The investigation of alumina-carbon materials as well as alumina-coated materials show that a secondary alumina layer was formed due to the carbothermic reduction of alumina in the base material and the reoxidation of the gaseous aluminium sub-oxide species at the interface between the sample and the steel-melt with a thickness of 150 till 400 nm. The same layer was also found at the surface of the alumina coating. Endogenous particles with characteristically shape were deposited on both investigated surfaces.

The new formed layer was found to be highly reactive, and inclusions with similar chemistry were adsorbed onto this secondary surface due to the similar high interfacial energy.

The experiments with the aid of the steel-casting simulator offer the opportunity to investigate samples after steel contact without the presence of a closed steel film and the resulting preparation difficulties for the following investigations via electron microscopy. The influence of the atmosphere (oxidation) could be excluded for al experiments due to the presence of a fully controlled argon atmosphere.

REFERENCES

[1] Apelian D, Mutharasan R, Ali S. Removal of inclusions from steel melts by filtration, J. Mater. Sci. 20 (1985) p. 3501-3514.

[2] Davila-Moldonado O, Adams A, Oliveira L, Alquist B, Morales RD. Simulation of fluid and inclusions dynamics during filtration operations of ductile iron melts using foam filters, Mat. Transactions B, 39 (2008) p. 818-839.

[4] Emmel M, Aneziris CG. Functionalizasion of carbon-bonden alumina filters through the application of active oxide coatings for steel melt filtration, J. Mater. Res. (2013) http://dx.doi.org/10.1557//jmr.2013.56.

[3] Aneziris CG, Dudczig S, Hubalkova J, Emmel M, Schmidt G, Alumina coatings on carbon bonded alumina nozzles for active filtration of steel melts, Ceram. Int. 39 (2013) p. 2835-2843.

[4] Dudczig S, Aneziris CG, Dopita M, Rafaja D, Application of Oxide Coatings for improved steel filtration with the aid of a metal casting simulator, Adv. Eng. Mat. 15 (2013) p. 1177-1187.

[5] Aneziris CG, Dudczig S, Emmel M, Bereck H, Schmidt G, Hubalkova J, Reactive filters for steel melt filtration, Adv. Eng. Mat., 15 (2013) p. 46-58.

[6] Dudczig S, Aneziris CG, Emmel M, Schmidt G, Hubalkova J, Bereck H. Characterisation of carbon-bonded alumina filters with active or reactive coatings in a steel casting simulator, Ceram. Int. 40 (2014) p. 16727-16742.