

REACTIVE FILTER COLLECTORS BASED ON CALCIUM ALUMINATES WITH CARBON FOR CLEAN STEEL APPROACHES

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ABSTRACT

New carbon-bonded filters with coatings based on calcium aluminates were developed. The samples were tested for 10 s in contact with a steel melt containing endogenous inclusions at 1650°C, in order to explore the impact of these materials on the filtration process. Investigation of the filters after the test was carried out by optical and scanning electron microscopy. In addition, steel samples were analyzed with a special automatic SEM. The population of detected inclusions was classified in terms of size and chemistry.

Keywords: Ceramic foam filters, Calcium aluminates, Non-metallic inclusions

INTRODUCTION

Non-metallic inclusions in cast metal parts usually have a detrimental effect on the properties of the components. They can cause internal cracks, slivers, or blisters in final rolled products. Moreover, large macro-inclusions as well as inclusion clusters severely degrade the mechanical properties^[1]. Especially for safety relevant components, it is crucial to improve the cleanliness of the metal melts: high purity can be achieved by using a filtration process after the ladle treatment^[2]. In particular, carbon-bonded alumina filters are increasingly used by steel foundries. However, their potential regarding material characteristics and filtration efficiency has not been fully exploited yet.

The material buildup on a carbon-bonded alumina filter, after a 60 s immersion test in a steel melt at 1650°C, as discussed by Dudczig et al., generally presents the following structures (from the center of a strut to the surface)^[3]:

- A. Unaffected carbon-bonded substrate
- B. Decarbonized layer of partially sintered alumina
- C. Oxide functional coating -- from the production process (optional)
- D. Secondary, thin alumina layer -- from the in situ reaction
- E. Dense collection zone mainly consisting of sintered, polyhedral endogenous alumina inclusions
- F. "Coral-like" zone consisting of endogenous alumina particles in complex shapes.

In terms of this contribution, calcium aluminate coatings containing carbon were explored. Such kind of functional coatings on a carbon-bonded filter substrate may provide a number of advantages for capturing fine alumina and calcium aluminate inclusions. Calcium has a low solubility in molten steel (300 ppm), high vapor pressure (1.84 atm at 1600°C), and reacts violently with air due to its affinity for oxygen^[4]. When these compositions come in contact with steel melt following mechanisms could be expected:

- I) The calcium aluminates react with the carbon, forming calcium aluminate suboxides or (less likely) also calcium, which are deposited on a calcium aluminate, partially decarburized zone in contact with the metal melt. Next, a thin active calcium aluminate layer is generated thanks to the reaction of these suboxides with the oxygen of the steel

melt. This layer between the decarburized zone and the steel melt is contributing as an active collector for endogenous inclusions^[5].

- II) In addition, the high vapor pressure of calcium with an associated bath stirring promotes collision and coalescence of the alumina fine inclusions in the melt. These non-buoyant inclusions usually need to cluster on their own before they can be separated in the slag. As a consequence, the removal of these inclusions from the steel is enhanced.
- III) Depending on the applied composition of calcium aluminates, the softening point and/or the melting point of the mixture can be adjusted in order to increase the filtration efficiency by increasing the roughness of the thin active layer which copies the surface of the carbon-free calcium aluminate layer below. A higher roughness leads to higher wetting angle against the iron melt^[6], which promotes a higher agglomeration via collision of the fine inclusions.
- IV) Based on the softening of the thin active layer, the endogenous inclusions are trapped mechanically better during their collision on the active surface and more contacting surface is available for sintering and fixing of the inclusions on the surface of the thin active layer.

In the present contribution, carbon-bonded alumina filters with coatings based on calcium dialuminate and calcium hexaluminate were tested in contact with a steel melt at 1650°C. Before immersion, endogenous alumina inclusions were artificially generated, in order to simulate a filtration process. The inclusions remaining in the steel were thoroughly analyzed and classified by size and chemistry by means of a special scanning electron microscope.

MATERIALS AND METHODS

Filter production

The raw materials used for the preparation of the Al₂O₃-C filters were aluminum oxide (Martinswerk, Germany, 99.80 wt.% Al₂O₃, d₉₀ ≤ 3.0 μm), modified coal tar pitch powder (Rütgers, Germany, d₉₀ < 0.2 mm – used as a binder as well as a carbon source), fine natural graphite (Graphit Kropfmühl, Germany, 96.7 wt.% carbon, 99.8 wt.% < 40 μm), and carbon black powder (Lehmann & Voss & Co., Germany, carbon content ≤ 99.0 wt.%, ash content > 0.01 wt.%, primary particle size of 200-500 nm). The additives were ligninsulfonate (Otto-Dille, Germany – used as wetting agent and temporary binder), modified polycarboxylate ether (BASF, Germany – used as a dispersing agent), and alkylpolyalkyleneglycolether (Zschimmer & Schwarz, Germany – used as an antifoam agent). The carbon-bonded filters (10 pores per inch, 125 x 22 x 22 mm³) were produced via the Schwartzwalder process using a two-steps approach, according to the parameters described by Emmel et al.^[7]. After drying, the filters were heat treated in retorts filled with calcined petcoke (Müco, Germany) with a particle size between 0.2 and 2 mm, to approach reducing conditions. The maximum temperature of 800°C was reached with a heating rate of 1 K/min, additional dwell steps of 30 min for every 100°C, and a final holding time of 180 min at 800°C.

The compositions presented in the following are protected by patent (application number EP 16305289.7; extension number PCT/EP2017/056296). The raw materials used for the preparation of the coatings were CA2 (Kerneos, France, >99 wt.% Calcium dialuminate, $d_{90} \leq 15.0 \mu\text{m}$), CA6 (Kerneos, France, >99 wt.% Calcium hexaluminate, 0-0.020 mm $d_{50} \leq 6.0 \mu\text{m}$), and modified coal tar pitch powder (see above – used as a binder). The additives were (see above) ligninsulfonate, modified polycarboxylate ether and alkylpolyalkylene-glycoether in the same concentrations as for the filters. For each composition the spraying slurry was prepared by means of mechanical stirring and applied with a spray gun in a dedicated chamber. After application and drying of the coating, the filters were thermally treated again under reducing conditions (see above) in order to achieve the bonding of the coating and close some residual porosity and cracks.

Melting experiment

A metal casting simulator (Systec, Germany) located at the Institute of Ceramic, Glass and Construction Materials in Freiberg was used to evaluate the purification behavior of the functionalized $\text{Al}_2\text{O}_3\text{-C}$ filters. Before melting, the casting simulator was evacuated to a pressure of 2 mbar and filled with Ar 4.6 (purity = 99.996 %). The whole procedure was performed twice. Next, ≈ 40 kg of commercially available 42CrMo4 steel (AISI 4142) were melted in a special crucible: this consisted of hydratable alumina-bonded alumina/alumina-magnesia-spinel material, without any silica, calcia or further additions (to prevent unwanted reactions during the experiment), presintered at 1600°C for 2h. The oxygen content and the temperature of the steel melt were measured with a p_{O_2} /T-sensor system (Heraeus Electro-Nite, Germany) at different stages of each test. Before the immersion of the filter samples, defined alumina impurities were created in the steel melt according to the procedure described by Dudczig^[3]. Once the desired temperature was reached, 0.5 wt.% (related to the steel mass) of an iron oxide mixture were added. Accordingly, the dissolved oxygen rose from 20-30 ppm up to 60-70 ppm. At this point, endogenous alumina inclusions were generated by adding 0.05 wt.% (again related to the steel mass) of pure aluminum metal to the melt. Only about 10 ppm [O] were detected after this step. Finally, the ceramic foam samples were dipped into the melt (at a temperature of $\approx 1650^\circ\text{C}$) and rotated with 30 revolutions per minute for 10 s. All “finger-tests” were carried out under fully controlled argon atmosphere. At the end all samples were removed from the melt and cooled down in a chamber under argon in order to prevent oxidation of the carbon fraction.

Inclusion analysis

During the experiment, cylindrical steel samples with ≈ 3 cm diameter and 1 cm height were extracted from the melt, once after the steel treatment and once after the filtration test. These metallographic specimens were mounted, carefully grinded and polished down to 1 μm . Next, the samples were analyzed by means of a special, automatic SEM (FEI, USA): areas of approximately 110 mm² were scanned for about 8 h. Inclusions $> 0.6 \mu\text{m}$ were detected using a BSE (back-scattered electron) detector based on contrast difference with the steel matrix. For each found particle the AFA (automatic feature analysis) included position, geometry, orientation and chemical composition, this last one being carried out by EDS (energy-dispersive X-ray spectroscopy). Afterwards, the inclusions were classified by composition according to the rule-file presented in Tab. 1. Rule-files are not commonly available and must be developed using reference specimens of known composition. In

the table, “Dirt” refers to spots with very high carbon content, which could indicate the presence of organic residuals on the sample. “Fe scratch” relates to abrasions left by the preparation process. “Others” refers to any composition that did not match our rule-file. Iron oxide was likely formed by corrosion of the surface after removal of an inclusion during the polishing process.

Table 1: Rule file used for the automatic SEM analysis to classify the inclusions found in the solidified steel samples.

Chemical class	Element content [mol%]
Al_2O_3	$\text{Al} > 8$ and $\text{O} > 8$ and $\text{Mn} < 10$ and $\text{S} < 8$ and $\text{Ca} < 5$
Ca-aluminate	$\text{Ca} > 10$ and $\text{Al} > 5$
Mg-spinel	$\text{Al} > 8$ and $\text{Mg} > 0$ and $\text{S} < 5$ and $\text{Ca} < 5$
Al-Mn-Mg-Fe-Ca-silicate	$(\text{Si}/\text{Al}) > 0.4$ and $(\text{Al} + \text{Mn} + \text{Mg} + \text{Ca}) > 10$
SiO_2	$(\text{Si}/\text{O}) \geq 0.4$ and $(\text{Si}/\text{O}) < 6.2$ and $\text{Al} < 3$ and $\text{Mg} < 3$ and $\text{Ca} < 3$ and $\text{K} < 3$ and $\text{Mn} < 5$ and $\text{S} < 10$
MnO-MnS	$\text{Mn} > 8$ and $(\text{Mn}/\text{S}) > 2$ and $\text{Al} < 20$ and $\text{Si} < 5$ and $\text{Ca} < 5$
CaO-CaS	$\text{Ca} > 5$ and $(\text{Ca}/\text{S}) < 2$
Dirt	$\text{C} > 10$
Fe-oxide	$\text{Fe} > 60$ and $\text{O} > 20$ and $(\text{Si} + \text{Al} + \text{Mn} + \text{Mg} + \text{Ca} + \text{Na}) < 10$
Fe-scratch	$\text{Fe} > 90$
Other	True

RESULTS AND DISCUSSION

The carbon-bonded filters were able to withstand the strong thermal shock and high temperature conditions. According to our sensor, the dissolved oxygen only rose up to about 30-40 ppm after the test (i.e. to an acceptable value), in both cases. No macroscopic damage was observed after the test and only the areas which were in direct contact with the melt showed a color change from dark to light gray: this was related to decarburization of the surface and formation of a new phase at the contact with the steel melt.

Optical micrographs of the filters after the immersion tests are presented in Figs. 1-4 (only the affected part is shown). Some damage in the form of cracks was observed, as when testing uncoated carbon-bonded filters for 10 s. However, thanks to the formation and progressive growth of new layers, cracks are usually sealed for ≥ 30 s contact time. Moreover, some steel (mainly in the form of spherules) was collected on the surface of both samples. Interestingly, the surface of the CA2-C filter looked quite rough in comparison to the other sample. This would suggest a different (re)activity of the respective coating with this steel and the generated inclusions.

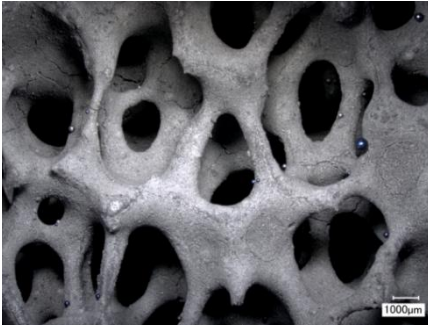


Figure 1: Overview of the CA2-C filter surface after 10 s of contact with the steel melt.



Figure 2: Detail of the CA2-C filter surface after 10 s of contact with the steel melt.



Figure 3: Overview of the CA6-C filter surface after 10 s of contact with the steel melt.

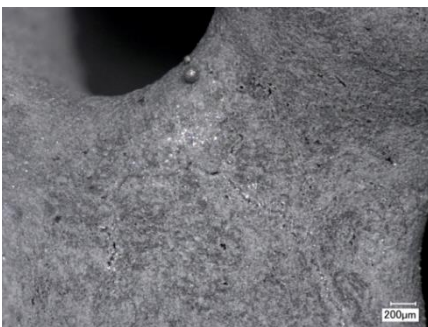


Figure 4: Detail of the CA6-C filter surface after 10 s of contact with the steel melt.

SEM micrographs of the filter surfaces after contact with the steel melt are presented in Figs. 5-8. The CA2-C filter showed, as expected, a higher roughness than the CA6-C filter. Interestingly, a lot of pores infiltrated with steel (white spots) were found. The rest of the surface consisted of polyhedral particles partially sintered together. The EDS detector revealed Al, Ca and O as main constituents of this zone. The CA6-C

surface was smoother and did not show any major porosity with entrapped steel. The interesting morphology of the CA2-C surface could in our opinion be related to the high Ca content of the coating: gaseous calcium (Ca boils at 1484 °C) and/or suboxides were produced from the reaction between the calcium aluminate and the steel melt, with the formation of pores which were readily infiltrated by liquid metal. From a cross sectional view, the applied coating (layer C) with a thickness of approximately 40 μm could be easily recognized over the substrate material. On both samples the thin secondary layer D was also observed, although only in a few spots. Fig. 8 shows that this layer effectively collected some nano-inclusions. These exhibited a dendritic shape and were found in clusters. We believe that these particles are the actual endogenous inclusions produced by our treatment before the immersion test^[8]. According to Dekkers, at very high oxygen and aluminum supersaturation, growth of alumina inclusions becomes unstable and the crystal corners grow along the supersaturation gradient, which may result in the formation of dendrites^[9]. On the other hand, layers E and F mainly consist of plate-like particles that should derive from the reaction of the filter material at the interface with the molten steel, as described in the Introduction.

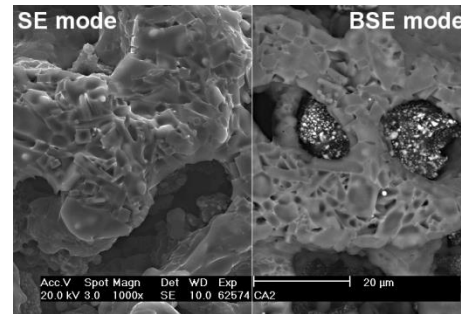


Figure 5: CA2-C filter surface after 10 s immersion test.

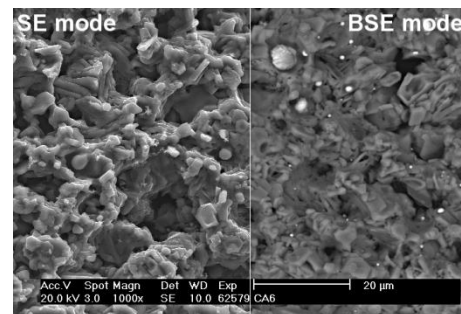


Figure 6: CA6-C filter surface after 10 s immersion test.

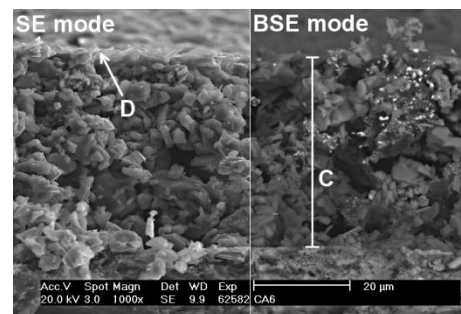


Figure 7: Strut section of the CA6-C filter after 10 s immersion test.

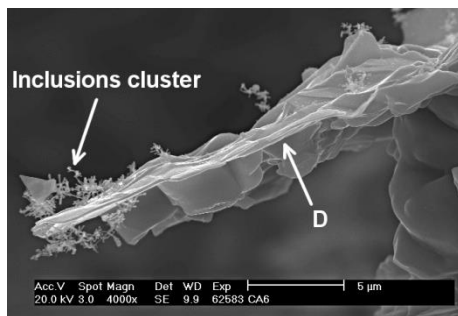


Figure 8: Detail of CA6-C filter with layer D and collected inclusions.

The inclusions found by means of automatic SEM on the steel surfaces are presented in Tab. 2, classified by chemistry. “After treatment” represents the status after oxide/Al addition, but before filter immersion. It has to be noted that these numbers represent the particles left in the solidified steel after testing the filters in the steel casting simulator, hence lower values would indicate a better purification efficiency, assuming that our steel samples were significant. Since “Dirt”, “Fe-oxide” and “Fe scratch” do not represent actual inclusions, they are not listed here. In addition, the major constituents of the “other” inclusions were Fe, O and Si: therefore, they likely derive from the preparation process and can be ignored. As expected, most of the inclusions detected after the steel treatment were classified as aluminum oxide. Silicates were also present in a lower amount. For the most part, all inclusions showed a surface area $<20 \mu\text{m}^2$. It was clearly observed that the use of a filter had a very positive effect on the steel purity. Considering only the Al_2O_3 class, the filtration efficiency of both samples was close to 100%. Calculations predict a maximum filtration rate of only 24% and 18% for 10 and 30 ppi filters, respectively^[10]. It should be noted, though, that the model by Asad et al. does not yet consider the presence of gas bubbles in the melt or any chemical interaction between ceramic filter and inclusions. Moreover, within the model the prismatic filter is not rotating as in the real setup. The model will be improved in the future.

Table 2: Number of inclusions found in the steel samples by automatic SEM analysis, classified by chemistry.

Chemical class	Inclusions per cm^2			
	After treatment, pre filter	After CA2-C 10 s	After treatment, pre filter	After CA6-C 10 s
Al_2O_3	132	4	408	1
Ca-aluminate	0	1	0	0
Mg- spinel	4	0	0	0
Al-Mn-Mg-Fe-Ca-silicate	11	7	50	2
SiO_2	1	2	1	0
MnO-MnS	0	0	0	0
CaO-CaS	1	0	1	0
Other	56	33	143	29

CONCLUSIONS

Carbon-bonded alumina filters were functionalized with a coating based on calcium aluminates, CA2 and CA6 respectively. During the test in contact with molten steel at $1650 \text{ }^\circ\text{C}$, the filters developed different structures, with the

CA2-C sample showing a high porosity with entrapped steel. Partially sintered polyhedral particles containing Ca, Al and O were found on both surfaces. In addition, a thin secondary layer was also detected. After 10 s of contact, fine endogenous inclusions (artificially generated before the test) were collected especially on the CA6-C surface. The steel analysis after the immersion test indicated that both compositions can deliver excellent filtration efficiencies.

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