CARBON-BONDED ALUMINA FILTERS FOR STEEL MELT FILTRATION BY A GEL-CASTING PROCESSING ROUTE BASED ON SODIUM ALGINATE

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ABSTRACT

The use of carbon-bonded alumina filters became a popular approach to increase the purity of steel by removing non-metallic inclusions from the melt. However, established filter processing routes such as the replica technique are restricted with regard to the mechanical strength and the pore structure of the produced filter systems. In this study, a novel gel-casting process is presented as a viable alternative. The desired filter structures have been casted using a water-based alumina-carbon slurry with sodium alginate as gelling agent. By pumping the material into a watery solution of calcium chloride dihydrate, the alginate forms a solid gel. This allows the computer-assisted manufacturing of three-dimensional lattice structures consisting of a continuous filter strut. The produced filter structures were immersed in a steel melt at 1585 °C. Afterwards, the microstructure and the chemical composition of the filter surface were characterized by digital light microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The study showed that the developed processing route is suitable for the production of carbon-bonded alumina filters for steel melt filtration. The tested samples provided sufficient thermal shock resistance and refractoriness in contact with molten steel. Furthermore, in-situ formed layers and crystalline phases were found on the surface of the immersed filters. These observations prove the filter effect of the produced alumina-carbon structures. The novel processing route is very promising because it allows the production of full-strut filters with adaptable macro-porosity resulting in higher component strength and tailored melt flow conditions.

Keywords:
Carbon-bonded alumina, gel-casting, spaghetti filter, metal melt filtration, steel casting simulator

INTRODUCTION

The performance of high quality steel highly depends on its purity regarding the content of non-metallic inclusions. Therefore, high efforts are made to reduce potential sources of defects in order to ensure the best possible mechanical properties and the efficient processing of the casted steel [1]. The application of ceramic foam filters for the filtration of both molten ferrous and non-ferrous alloys became a very popular approach for reducing the amount of detrimental non-metallic inclusions due to their good cost-benefit-ratio [2]. However, the applied manufacturing process results in some crucial drawbacks regarding the final properties of the produced filters [3].

Ceramic foam filters are produced by the replication of open-celled polyurethane foams. Thereby, the polymer structure is coated with a ceramic slurry, dried and heated to the necessary firing temperature. During the heating process, the polyurethane template pyrolyzes and leaves a hollow filter strut consisting of the ceramic coating material. The formed inner voids show the same triangular cross-section as the struts of the original polymer foam. As a consequence, these sharp-edged cavities act as stress-concentrating areas resulting in reduced mechanical strength [3].

The used polyurethane foam templates also predefine the structure of the filter pore cells, which typically are described as pentagonal dodecahedron [4]. Of course, the open-celled foam structure highly influences the melt flow conditions in the filter and the resulting filtration efficiency. With the aid of numeric flow models, the optimal pore cell structure, which is necessary for achieving the best possible filtration efficiency, can be simulated [5]. However, the optimization of the filter structure is strictly limited by the replica technique.

With regard to these problems, other filter production techniques show high potential. Essock et al. presented an alternative processing route for the production of silicon carbide filters with large dimensions by extrusion of a continuous ceramic strand with the aid of suitable plasticizers (Fig. 1). Due to the solid filter strand without inner voids, the resulting so-called spaghetti filters showed very good mechanical properties and thermal shock resistance [6]. For steel melt filtration, there were attempts to adopt the technique also for carbon-bonded alumina material. However, the production failed because of the high elastic nature of the used composition. The extrusion of a continuous filter strand without tearing was not achieved due to the lack of plasticity despite the addition of plasticizers. Therefore, a novel gel-casting process based on sodium alginate was developed in order to enable the manufacturing carbon-bonded alumina spaghetti filters with solid struts and adaptable lattice architecture.

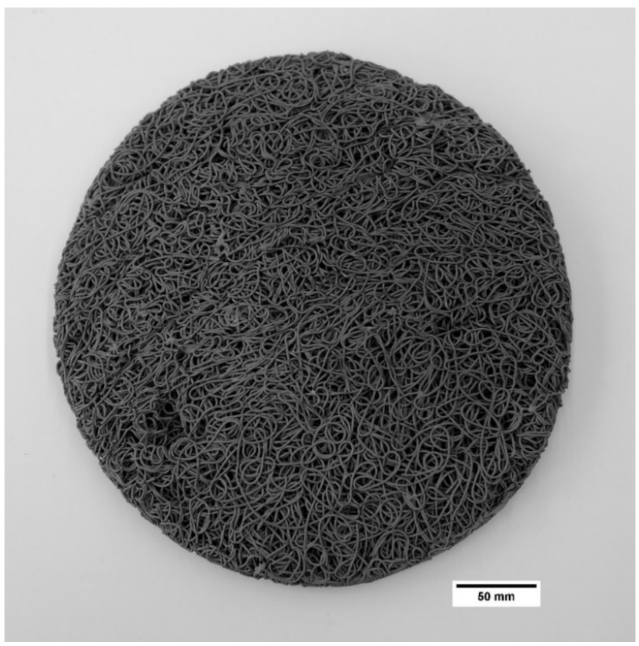

Fig. 1: Extruded silicon carbide spaghetti filter with chaotic pore structure [6].

Alginates are natural, non-toxic gelling agents and thickeners applied primarily in the food and cosmetic industry. The structure of the polymer consists of two types of monomers: α-L-guluronate (G) and β-D-mannuronate (M). By the combination of these monomers, different possible dimer blocks are formed. For the gelation by the incorporation of alkaline earth ions, especially blocks of α-L-guluronate monomers (GG-blocks) are of interest. Certain divalent ions such as calcium and barium ions are able to take the place of the original counter-ion such as sodium by ion exchange and connect the GG-blocks of two polymer chains. By this incorporation, a rigid three-dimensional network is formed

resulting in the stiffening of the former alginate dispersion. The linkage of two GG-blocks by divalent cations is also referred to as egg-box structure due to its typical shape [7].
The gelation process happens instantly if the slurry surface is in contact with solutions containing free calcium or barium ions [8]. Therefore, it is possible to create a continuous solid ceramic "spaghetti" by pumping the alginate-containing slurry into a solution of calcium chloride dihydrate. The created ceramic spaghetti can be used to form three-dimensional lattice structures for filtration purposes. Thereby, the producible strut diameter is limited because the gelation in the center of the slurry stream is inhibited by the decreasing ion diffusion rate.

EXPERIMENTAL

The main composition of the alumina-carbon slurry consisted of 66 % fine-grained alumina, 20 % coal tar pitch binder, 8 % carbon black and 6 % natural crystalline graphite. As gelling agent for the gel-casting process, sodium alginate was added.
Polyvinyl alcohol (PVA) was used as main temporary binder. Therefore, a concentrated solution of PVA was prepared by stirring at 80 °C for 6 hours. Afterwards, the mixture was diluted with deionized water to the desired concentration. The PVA solution as well as small amounts of a dispersing agent and a defoaming agent were added to the dry material and the resulting slurry was ball-mixed for 2 hours on a drum roller mixer.
The mixed slurry was de-aired for 10 minutes at 0.1 bar pressure and afterwards stirred at atmospheric pressure. After repeating this procedure three times, the slurry was ready to use. This degassing process was necessary to ensure the bubble-free pumping without tearing of the formed continuous spaghetti structure.
The experimental setup for the sample preparation comprised the peristaltic pump, the computer-assisted robot arm and the tank with the alkaline earth solution. The pump tube with a diameter of 1.6 mm was attached to the robot arm. In order to obtain a continuous gel-casted strand, the tube end was immersed into the calcium chloride dihydrate solution during pumping. After immersing the tube, the robot started the desired casting program. The completed structure was lifted out of the tank with the solution. Thereby, the used casting underlay has to be suitable for the process. It has to allow the drainage of excessive liquid, the transport of the sample and the unhindered dry shrinkage without damaging the structure. The filters were dried for 24 hours at room temperature.
The contact points of the dried spaghetti filters are not or only slightly connected because of the quick gelation and stiffening during the process. On the one side, this provides the unhindered shrinkage of the ceramic lattice structure without the formation of excessive stresses and subsequent cracks or deformation. However, the dried filters are very fragile in this state, even after the firing process. Therefore, an additional spray-coating was applied in order to interconnect the filter struts and to reinforce the structure. The carbon-bonded alumina slurry composition used in the projects of the Collaborative Research Center 920 was chosen as coating material [9]. In this way, the surface chemistry of the spaghetti filter equals that of the ceramic foam filters in previous works and the comparability is ensured. After drying the filters for another 24 hours at room temperature, the produced samples were fired in a petrol coke bed under absence of air at 800 °C for 3 hours. The final microstructure and the interface between the coating and the base material are shown in figure 2.
In order to evaluate the optimum solid content and alginate content of the slurry for the gel-casting process, different tests regarding the slurry rheology, filter form stability, material green strength and dry shrinkage were conducted. As a result, a slurry with 56 wt% solid content and 0.65 wt% alginate was most suitable for further tests.
Based on the results of the gel-casting tests, finger samples for the steel casting simulator with final dimensions of 25 x 25 x 150 mm were produced. The loop, which is required for the sample holder of the steel casting simulator, was created after the gel-casting by applying a cylindrical placeholder.

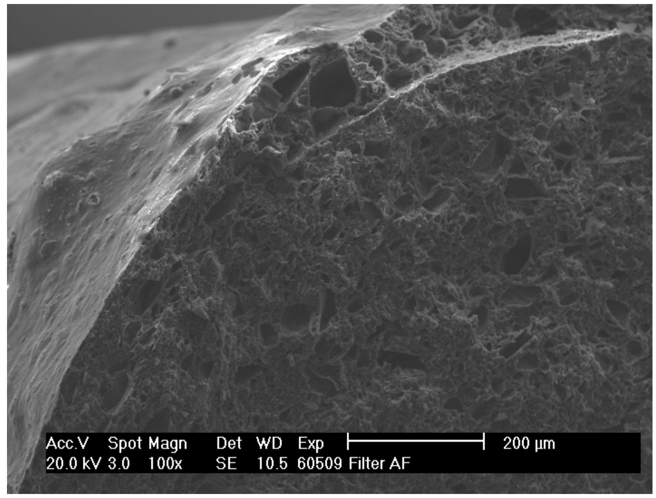

Fig. 2: Microstructure of a gel-casted carbon-bonded alumina filter strut with coating after heat treatment.

The steel casting simulator allows the melting and casting of steel under argon atmosphere as well as the immersion of prismatic samples into the molten metal. 31.6 kg of alumina-killed 42CrMo4 steel (17.225), which was heated to 1585 °C, was used for this test. The finger sample has been immersed in the steel melt without preheating and was rotated for 30 s at 30 rotations per minute. After the immersion, the filter was lifted out of the melting unit allowing the cooling under argon atmosphere to prevent the oxidation of the carbon.
One main aim of the test was to examine the thermal shock resistance of the produced structures in contact with steel. Additionally, the filtration effect in comparison to alumina-carbon foam filters was investigated. Therefore, the surface of the immersed and cooled filter was analyzed by digital light microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

It was possible to immerse the non-preheated gel-casted filter into molten steel without failure of the structure. This is due the good thermal shock behavior of carbon-bonded material. However, there were some cracks observed in the immersed filter. That means that some of the struts broke during the test due to thermal stresses, however, due to the lattice structure, the cracks did not lead to the complete failure of the filter. It is also possible that the cracks occurred after the actual immersion test and during the cooling stage.
Furthermore, it was shown that the steel did not infiltrate the whole filter structure. The filter core was not in steel contact until an immersion depth of approximately 25 mm. That means a certain ferrostatical pressure was necessary to penetrate the inner layers of the filter lattice. This behavior is observed only marginally for common 10 ppi foam filters. As a result, the spacing between the struts of the spaghetti filter should be increased in order to enable proper priming. Especially under industrial casting conditions, the insufficient priming or too high pressure drop can lead to problems such as the solidification of the steel.
The filter appearance changed after the immersion in steel. Thereby, the areas that were in steel contact showed a bright, rough surface (Fig. 3). As already observed by Dudczig et al. for carbon-bonded

alumina foam filters, a thin in-situ layer was formed [9]. Most likely, this layer consists of very fine-grained alumina deposits, which precipitate out of the steel due to the change in local chemistry. Zienert et al. described that the high carbon content of the filters in combination with the oxygen dissolved in the steel results in the formation of CO, which strongly disturbs the equilibrium conditions at the steel-filter-interface. Thermodynamically, the partial dissolution and precipitation of alumina in the steel is promoted resulting in a layer formation [10]. The content of oxygen dissolved in the steel decreased from 32.873 ppm to 31.484 ppm during the test indicating its contribution to the layer formation.

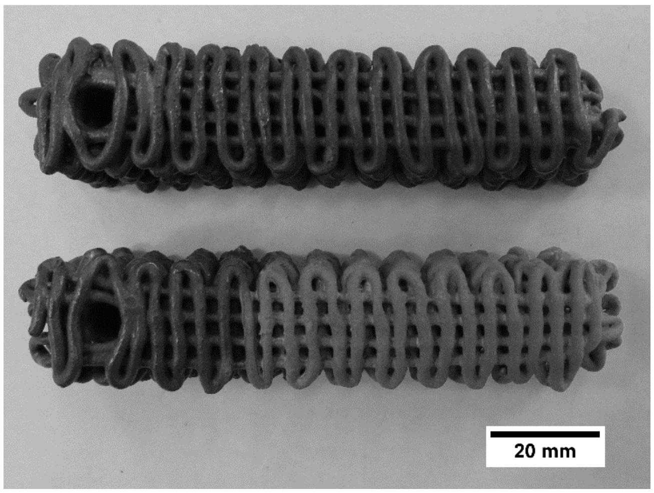

Fig. 3: Filter sample before (above) and after (below) the immersion test in molten steel.

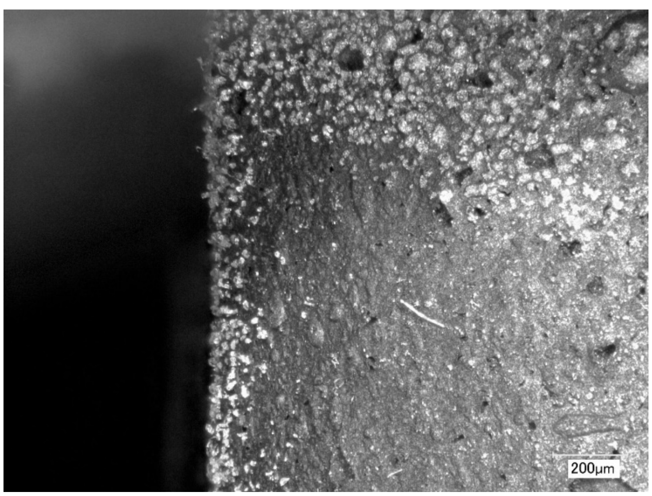

Fig. 4: Clear crystalline deposits on the surface of the in-situ formed layer.

Distributed on the surface of the in-situ formed layer, clusters of clear crystals were found (Fig. 4). XRD analysis of the filter material in steel contact compared to the filter material in atmosphere contact were conducted. The results show that there are larger peaks of α-Al_2O_3 for the immersed material in contrast to material that was not in contact with the steel melt. That indicates that the found deposits are alumina inclusions separated from the steel melt, as also observed for carbon-bonded alumina foam filters. However, it has to be noted that the partial decarburization of the carbon-bonded material also had an influence on the relative increase of the alumina fraction.

Fig. 5: SEM image (BSE mode) of a vermicular deposit.

Tab. 1: EDX analysis of the found vermicular deposits.

Element	Wt %	At %
Al K	26.40	23.98
Si K	00.95	00.83
S K	00.29	00.22
Cl K	02.64	01.82
Ca K	00.47	00.29
Cr K	01.06	00.50
Mn K	00.33	00.15
Fe K	29.01	12.73
Oxygen (calculated)	38.84	59.48

Beside clear alumina crystals, also some vermicular deposits were observed with the aid of SEM (Fig. 5). EDX investigations indicated that these deposits are rich in both iron and aluminum (Tab. 1). Thereby, the molar aluminum/iron ratio is approximately 2. This indicates that the found deposits were hercynite of the formula $FeAl_2O_4$. Additionally, the structures contained almost 2 at% chlorine. The chlorine originates from the gel-casting process with calcium chloride dihydrate as gelation initiator and was incorporated in the structure of the non-metallic deposits. It is possible that the chlorine had an effect on the formation of the found deposits.

CONCLUSIONS

In this study, it was shown that the new processing route is suited for the production of functional alumina-carbon filters for the steel melt filtration. The spaghetti filters possess solid struts without sharp-edged voids that lead to the formation of cracks and component failure. With the aid of computer-assisted techniques such as robocasting it is possible to create tailored cellular structures allowing the optimization of the flow conditions and the filter efficiency.

The tested filter sample did withstand the thermal shock occurring by the immersion in molten steel. However, the used lattice spacing seemed to be too narrow to ensure unhindered priming and infiltration under given conditions. As a result, a higher ferrostatic pressure was necessary to infiltrate the pore structure.

The test in the steel casting simulator revealed that an in-situ formation of thin films occurs at the interface between the filter material and the steel melt. On the surface of the formed layers, which most likely consist of fine alumina, clear crystalline deposits were observed. This is in agreement with previous investigations regarding the behavior of carbon-bonded alumina foam filters. However, there were also deposits with high iron and aluminum content, indicating the formation of hercynite with a certain chlorine content.

Future investigations should focus on the filtration behavior of the gel-casted material at different immersion times in molten steel allowing the direct comparison to carbon-bonded ceramic foam filters and the better understanding of the observed deposition mechanisms.

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