

Advanced Ceramic Filtering Materials: a Contribution to Clean Steel Technologies

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Non-metallic inclusions in cast metal parts remarkably influence their performance during application. It is well known that size, type and distribution of non-metallic inclusions in metals distinctly influence their fracture toughness, tensile strength, ductility and fatigue. For the last three decades ceramic foam filters have been applied successfully in steel foundries for metal products with superior properties. Excellent operating filter systems fulfil two basic functions which are a) removing impurities on millimetre, micron as well as submicron scale, and b) promoting a non-turbulent melt filling of the mould if they are applied correctly during operation especially in means of time dependent interactions according to the filter material contribution. At present, the formation mechanism as well as the kinetics of observed in situ layers on filters in contact with steel melt and their influence on the deposition of inclusions from the steel melt is a main focus of the Collaborative Research Center 920 of the German Research Foundation in Freiberg. In terms of this presentation the contribution of different in situ formed layers as a function of their chemistry, porosity, time of interaction with the steel melt and the kind of treatment of the steel will be demonstrated and discussed in case of functional surface filter coatings as well as coatings on crucibles. Theoretical models are proposed which confirm the experimental results in a special steel casting simulator as well as in real trials in a foundry.

Introduction

Non-metallic inclusions in cast metal parts remarkably influence their performance during application. It is well known that size, type and distribution of non-metallic inclusions in metal decrease dramatically the mechanical properties and especially the fracture toughness, the tensile strength, the ductility as well as the fatigue of the cast products resulting to excessive casting repairs or rejected castings [1]. In case of the oxide inclusions in steel melts, Wasai et al. assigned the dendritic, maple-like and polygonal inclusions to the group of the primary inclusions generated directly after adding aluminium in the metal melt [2]. In contrast, the network-like, coral-like and spherical inclusions, which are composed of alumina, hercynite and wüstite, are classified as secondary inclusions. The secondary inclusions are formed due to the lower solubility of oxygen in the melt as a function of the temperature above the liquidus temperature of the melt. In case of the sec-

ondary inclusions, the α -, γ - and δ -alumina modification are more frequently detected in steel melts.

In the last four decades, ceramic foam filters are successfully applied in iron and aluminium foundries for metal products with superior properties. Current filter systems fulfil two basic functions: a) remove impurities in millimetre, micron and submicron area, and b) promote non-turbulent melt filling of mould reducing possibility of reoxidation and erosion. Concerning the thermomechanical requirements of filter materials and filter structures, the thermal shock resistance, the refractoriness under load as well as sufficient mechanical strength at temperatures in the range of 1500 °C for iron and 1650 °C for steel are needed. In case of large castings, bigger casting surfaces as well as longer casting times with improved creep resistance of the filter components are required. For the steel melt filtration, filters based on partially stabilized zirconia have been established for the last two decades. In order to reduce shrinkage de-

fects as they appear in oxide filter systems, improve thermal shock resistance, increase the creep resistance and also achieve higher filtration capacities by reducing total filter costs, the carbon bonded ceramic technology has been successfully applied for steel filtration [3].

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Tab. 1 Technical data of nano-scaled additives

Nano-Scaled Additives	Purity [mass-%]	Specific Surface Area [m ² /g]
Carbon Nano-Tubes (CNTs), Timesnano/CN	>95,0	>40
Alumina Nano-Sheets (NS), Sawyer/US	95,0–99,8	9–40

The Collaborative Research Center (CRC) 920 "Multifunctional Filters for the Metal Melt Filtration – a Contribution to Zero Defect Materials" granted by the German Research Foundation in 2011 at the University of Freiberg aims to improve the mechanical properties of metallic materials for security and lightweight constructions, particularly for applications in mechanical engineering and vehicle construction with the aid of surface functionalised filter materials based on so called "active" as well as "reactive" coatings. In case of the "active" coatings, the same chemistry as the chemistry of the primary or secondary inclusions that have to be removed are generated on carbon bonded filters. On the other hand, "reactive" coatings react with the dissolved gas in the melt (for instance, oxygen in steel melts) and create inclusions above the liquidus temperature of the melt that are deposited on the filter [4, 5].

Experimental

The raw materials used for the preparation of the carbon-bonded alumina composition with the synthetic pitch Carbores® P as a binder as well as carbon source, were calcined alumina (99,80 mass-% Al₂O₃, ≤0,10 mass-% Na₂O) with a d₉₀ ≤3,0 μm (Martinswerk/DE), Carbores® P (Rütgers/DE) 0–20 μm, fine natural graphite grade AF 96/97 (99,8 mass-% <40 μm) with 96,7 mass-% carbon content (Graphit Kropfmühl/DE) and carbon black powder with a primary particle size of 200 to 500 nm (Lehmann & Voss & Co./DE). For the filter production prismatic templates based on polyurethane foam are used (pore size distribution in the range of 0,5–5 mm), with a porosity of 10 pores/ inch (ppi), a height of 22 mm and sides of 50 mm. The impregnation slurry consisting of 82 % solids was produced in a ToniMIX high shear mixer (ToniTechnik/DE). In the first step the powder components of the mixture were dry mixed for 5 min. After this the liquid components based on deionised water, Lignisulfonate T11B (Otto Dille/

DE), Castament VP 95L (BASF/DE) and Contraspum K 1012 (Zschimmer & Schwarz/DE) were added. Stepwise addition of the additional water led to a plastic mass, which was kneaded for another 5 min. Afterwards, the rest water was added and led to the formation of the slurry. For production purposes, the carbon bonded spray slurry consisting of 70 % solids was homogenised with a VISCO JET stirrer system (Inotec/DE). The same composition as the impregnation slurry was used, but a higher amount of deionised water was needed.

The pure alumina based slurry for the active spray coating was also produced in the stirrer system. In this case a wetting additive based on PPG (Sigma Aldrich/DE) was additionally added. The spraying was performed using a SATAjet B spraying gun and with a SATAjet B 1.0 E nozzle type (SATA/DE). Between foam and spraying gun, a constant distance of 20 cm as well as a constant pressure of the compressed air of 3 bar was maintained.

In case of the nano-engineered filter compositions, three filter versions were produced, a) impregnation slurry as Carbores filter with a spray slurry with 0,15 mass-% CNTs and 0,15 mass-% NS related to the solids, b) impregnation as well as spray slurry as Carbores filter with 0,15 mass-% CNTs and 0,15 mass-% NS related to the solids, and c) impregnation as well as spray slurry as Carbores filter with 0,3 mass-% CNTs related to the solids. The nano-scaled additives were added in several steps during mixing. The technical data of the nano-scaled additives are listed in Tab. 1.

After each impregnation as well as after each spraying step, all samples were dried at 25 °C for 12 h. Dried samples without any nano-scaled additives as well as without an active coating were cooked in a retort filled with coke breeze at 800 °C for 180 min. The heating profile was 1 K/min, and at each 100 K step, a 30 min holding time was programmed. Taken into account the contribution of Roungos et al., the carbon bonded filters with nano-scaled addi-

tives were coked at 800 °C under reducing conditions [6]. For the production of the carbon filters with the alumina based active coating, the Carbores substrate filter was first coked at 800 °C in advance, the active spray coating was applied at room temperature and then dried, and the composite filter was then coked at 1400 °C for 300 min also in a retort filled with coke breeze under reducing conditions. The determination of the cold crushing strength (CCS) was carried out at the universal testing machine TT 2420 (TIRA GmbH/DE), with a pressure cell of 20 kN. The speed adopted was 3 mm/min until a counteracting force of 5 N was reached. This was the switch-point, starting from which the speed was regulated to 1 N/mm²/s. When a loss of strength of 80 % was reached, the measurement was terminated. The open porosity of the struts of the coked Carbores filter was measured with the aid of a mercury porosimeter.

The microstructural phase evaluation of as coked fracture surfaces was carried out by means of scanning electron microscopy (SEM) with the implementation of electron backscatter diffraction analyses (EBSD) in combination with energy dispersive X-ray spectroscopy (EDS). The investigation was carried out in the scanning electron microscopes Philips ESEM and Philips XL30 equipped with an EBSD system TSL from Edax/Ametek.

The metal casting simulator located at the Institute of Ceramic, Glass and Construction Materials in Freiberg (Systec/DE) was used to compare the filtration behaviour of the uncoated and coated filters during very short operation times. A 10 ppi prismatic ceramic foam sample based on a template of geometry 125 mm × 20 mm × 20 mm was fixed at a special sample holder in a gas tight sewer port above a melting crucible. The used apparatus has been presented in detail by Aneziris et al. in [4]. In the present work, a so-called "finger test" was performed according to the procedure described by Dudczig et al. [5]. All tests were carried out under fully controlled argon atmosphere. ≈40 kg of commercially available 42 CrMo4 steel (AISI 4142) were melted under Ar in a special hydratable alumina-bonded alumina/alumina–magnesia–spinel crucible not containing any silica, calcia or further additions, in order to prevent unwanted reactions with the crucible

material during the experiment. The oxygen content and the temperature of the steel melt were measured in situ with a p_{O_2}/T -sensor system Celox (Heraeus Electro- Nite/DE) for the duration of each test. To create defined alumina impurities in the steel melt, 0,5 mass-% (related to the steel mass) of an iron oxide mixture were added.

The commercial product (Mineralmühle Leun/DE) consists of 75 mass-% hematite and 25 mass-% magnetite. After reaching a temperature of 1650 °C, the oxide mixture was added directly to the melt and an increase of the dissolved oxygen from around 10 ppm up to around 60 ppm was detected. At this point, the endogenous alumina inclusions were created by adding 0,05 mass-% (related again to the steel mass) of pure aluminium metal to the melt. Accordingly, the dissolved oxygen content fell back close to the starting value. After this step the prismatic sample, without any preheating, was dipped 60 mm into the steel melt through the sewer port and rotated for 10 (or 60) s at 30 rpm inside the melt. The filter was next removed from the melt and cooled down in a chamber under argon in order to prevent oxidation of the carbon, which would surely occur if the hot sample were left in contact with a normal ambient atmosphere. The influence of impurities from refractory materials was almost eliminated by using one crucible per melt. The distribution and chemical composition of the inclusions of the steel before and after the application of the filter materials were determined by an automatic SEM called Aspek (FEI/US). Thereby, a BSE detector identifies inclusions, which were larger than 1 μm , due to the different contrast compared to the steel matrix. Afterwards, each particle was characterized by an automatic feature analysis (AFA) that includes EDX, too. Thereby, position, geometry, orientation and chemical composition were determined.

Results and discussion

Mercury porosimetry measurements indicated that the open porosity of the struts of the Carbores filter reach values of 30 vol.-%. At this point we should underline that Carbores® P on the one hand is melting at approximately 238 °C and is infiltrating the pores of the matrix (this contributes to improved mechanical proper-

Tab. 2 Properties of Carbores filters with and without an alumina based active coating as well as nano-engineered compositions

Coked at 800 °C and 1400 °C	10 ppi	Strut Thickness [μm] Carbores Filter/Alumina Coating	CCS [MP]
	Carbores filter	300/0	0,33 \pm 0,04
Carbores filter + thin alumina coating	300/80	1,11 \pm 0,16	
Coked at 1000 °C	10 ppi 300 μm /30 μm		
	Carbores filter, only spray slurry with CNT + alumina NS		0,4 \pm 0,1
	Carbores filter, impregnation + spray slurry with CNT+ alumina NS		0,5 \pm 0,1
	Carbores filter, impregnation + spray slurry with CNT		0,8 \pm 0,4

ties). On the other hand, 15 vol.-% of the Carbores® P amount to organics that produce open pores during coking. In Tab. 2, the CCS strengths related to the weight and the strut thicknesses are listed. It is obvious that the alumina based active coating contributes to a higher strength. The combination of the two types of nano-scaled additions led to high mechanical strengths accompanied by low deviations. With the aid of the EBSD, the Al_3CON phase has been identified. With respect to the in situ formation of the new Al_3CON phase, the higher mechanical strengths are attributed to the chemical interconnecting phase of Al_3CON , which is assumed that contributes to a bonding between the oxide alumina filler and the carbon. Similar results have been reported by Roungos and Aneziris [6]. Recent studies in the special designed steel casting simulator have shown that the car-

bon and the alumina of the carbon-bonded alumina material react when immersed in a steel melt (which contributes catalytically), likely producing suboxides which move as gas towards the steel melt and forming a new thin, dense alumina layer in situ by catching the oxygen of the steel melt. Thermodynamic studies have in addition suggested a partial dissolution of alumina and carbon in the steel at the interface, followed by the reaction of this liquid with some fresh steel and the precipitation of the secondary alumina layer [7]. The new formed layer is consequently quite efficient in removing these particles from the melt, and the faster this layer is generated the better the trapping efficiency for the inclusions of the filter is. At this point we should also underline that not only suboxides are generated but also CO-bubbles which can also contribute via flotation to the filtration.

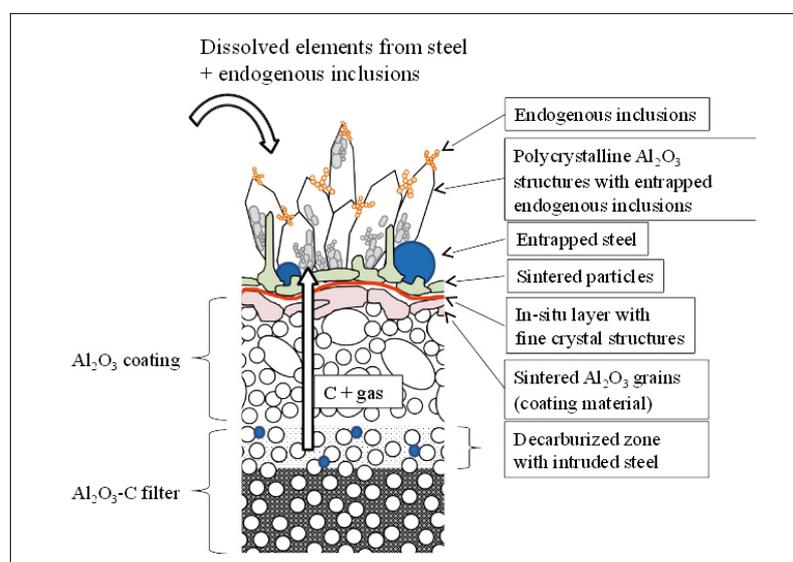


Fig. 1 Schematic principle of the formed layer buildup on the filter surface after Schmidt et al. [8]

Tab. 3 Number of inclusions remaining in solidified steel after immersion trials, classified by size; sample “0 s immersion” refers to a trial, during which molten steel was pretreated, but no filter immersed [8, 9]

Immersion Time [s]												
Number of Inclusions [per cm ²]												
Inclusion area [μm ²]	0,1–1	1–3	3–5	5–10	10–20	20–30	30–50	50–80	80–130	130–200	200–500	Total
Measurements of inclusions of frozen steel in crucible, Carbores filter with pure alumina coating												
0	338	488	223	255	80	10	2	0	0	0	0	1396
10	52	94	60	81	67	19	14	8	3	2	3	403
60	62	115	66	114	84	23	10	5	2	1	0	483
Measurements of inclusions of frozen steel in crucible, Carbores filter with nano-engineered coating based on CNTs and NS												
10	9	32	11	5	1	0	0	0	0	0	0	58
60	80	154	87	136	154	86	50	15	6	0	0	768

In Fig. 1 the schematic principle according to Schmidt et al. [8] is illustrated.

In Tab. 3 the populations of inclusions in steel after the immersion of different functionalised filters are listed in means of “clean steel filtration technology”.

According to Tab. 3, the active alumina coating improves the purity of the steel in the range of 70–84 % depending on the class of the inclusions in means of their inclusion area and in case of the nano-engineered surface filtration efficiencies up to up to 96 % can be achieved respectively.

Conclusions

New filter system approaches with functionalised surfaces have been demonstrated. The reinforcing of the carbon bonded compositions due to the nano-scaled additives is a first step for filter production with higher filtration capacities and bigger dimensions. Further the nanoscaled surface coating increases the reactivity for the in situ formation of the alumina thin layer which contributes as a collector.

As a result high filtration efficiencies are expected in short casting times [10]. The evaluation in real foundries will be explored in terms of the Collaborative Research Center 920.

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