CONTRIBUTION OF MOLTEN METAL FILTERS WITH THERMAL AND SLIP SPRAYED ALUMINA COATINGS TO THE CLEANLINESS OF STEEL

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ABSTRACT

Ceramic filters play an essential role on the cleanliness of cast steel parts as they calm the fluid steel flow as well as interact with the inclusions of the molten steel. A coating on such a filter is able to increase their strength and efficiency at catching inclusions. In this study, commercial Al_2O_3-C filters were coated with an alumina slip using cold spraying technology, and also with a flame spray technique. In comparison to commercial Al_2O_3-C filter, the microstructure of the coatings has been investigated by light microscopy and Scanning Electron Microscope (SEM), and the phase composition has been analyzed by X-ray diffraction. Furthermore, the effect of the filters with and without coating on the cleanliness of steel was evaluated in a steel casting simulator by immersing and rotating the filters into molten steel at 1580 °C for 20 seconds. After contact with molten steel, the surface of the filters has been analyzed. The alumina coating interacts with the Alumina-C filter substrate and steel forming an in situ alumina-rich layer, which promotes the deposition of inclusions during casting. This interaction also causes degassing of filter compounds which influences the steel grade as well. In contrast, flame spraying results in a coating which has a low porosity and hence, prevents any interaction of the filter substrate with the molten steel. Thus, a thermal spray coating is recommended for filtration of cast products with a high demand on cleanliness.

Keywords: Ceramic foam filters, alumina, coating, flame spraying, steel melt

INTRODUCTION

The steel casting industry is facing increasing pressure to produce clean, high-quality products. The cleanliness of the steel melt has a strong impact on the properties of cast steel parts. Nonmetallic inclusions, endogenous and exogenous, composed of oxides, carbides, nitrides and sulfides, remarkably influence mechanical strength, fracture toughness, deformation behavior, and resistance to fatigue [1]. Exogenous inclusions are known to originate from re-oxidation products and interaction with slags and refractory linings. Some endogenous inclusions precipitate during cooling and solidification; others are immediately formed as a result of the deoxidation process. For example, a high proportion of endogenous alumina particles are formed if aluminum is used as the deoxidation agent [2]. In addition to Al, steel can be deoxidized using Si, Fe–Al, Fe–Si, Ca–Si, Ca–Al, Ti, Fe–Ti, or Zr. All these deoxidation agents form fine oxide inclusions, which may not float up into slag if their particle size is below 30 µm [3]. Ceramic foam filters have been used in steel casting applications for several years to facilitate turbulence reduction on mold filling as well as ensure the requirements of high purity metal castings by removing nonmetallic inclusions and slag. Open-cell foam filters are produced using the replica process by impregnating foamed polyurethane with a ceramic suspension, squeezing out the excess suspension, drying, and firing the filters. The ceramic suspensions are composed of zirconia, alumina, magnesia, lime, mullite, zircon, silica, silicon carbide, or carbon-bonded alumina; zirconia and alumina-C are mainly used for steel filtration. Alumina-C filters exhibit higher creep resistance and provide very low weight and thermal mass. Khanna et al. have shown that during steel filtration reactions between the filter-compounds alumina and carbon, and steel take place [4]. This interaction leads to CO gas generation, carbon pick up of the steel, and the formation of new secondary phases, and is referred as the carbothermic reduction in molten steel [5]. Using the example of an Al_2O_3-C submerged nozzle, the carbothermic reduction leads to the buildup of alumina deposits when submerging the nozzle in an aluminum-killed steel. In contact with the hot face, a decarburized area is formed due to formation of CO. Consequently, CO is liberated into the metal, increasing the carbon and dissolved oxygen contents. This leads to precipitation of alumina at the interface between the steel and the nozzle, and a vitreous phase is formed by volatilization and oxidation reactions. At this surface layer alumina formation by oxidation of aluminum of the steel by CO takes place [6]. Aneziris et al. have compared alumina-coated nozzles with uncoated ones. The nozzle with an alumina coating showed increased amount of endogenous and exogenous inclusions as well as steel particles [7]. Correlating the clogging behavior to filtration efficiency of molten metal filters, this effect may increase the filtration of Al-rich inclusions from molten steel. In order to increase the filtration efficiency and the steel cleanliness, existing steel filtration techniques have to be enhanced, and new materials and methods developed. However, alumina-graphite refractories in contact with steel melt increase the carbon and silicon content of the cast steel parts. According to Poirier et al., the permeability of a refractory plays an essential role on the alumina buildup and an alumina coating promotes the buildup of alumina inclusions on the filter [6]. However, if a barrier is created on the surface, the diffusion of gases will be avoided, which will reduce interaction of the filter-compounds with steel. Hence, the aim of this study was to evaluate the effect of a porous and dense alumina top coating applied on an Al_2O_3-C-filter on the steel melt filtration mechanism.

MATERIALS AND METHODS

Carbon bonded Al_2O_3-C ceramic foam filters composed of 70 wt-% Al_2O_3 and 30 wt.-% carbon were used as both substrate and reference filter material. The filters had a size of 125 x 25 x 25 mm^3 and a macro porosity of 10 ppi (pores per inch). In order to investigate the filtration efficiency, the Al_2O_3-C reference filters (sample "AC") were coated with an Al_2O_3 coating via a cold spray technique (sample "AC+A CS") and alternatively using a thermal spray technique (sample "AC+A FS"). In order to prepare the slurry for cold spray coating, 65 wt.-% reactive alumina, 35 wt.-% deionized water and additives were mixed. The slurry was then sprayed on the "AC" filter. Detailed information on the slurry composition and coating process can be found in Emmel et al. [8]. The spraying took place on five sides of the filter, whereby the sides were sprayed for 6 s with a determined flow rate of 40 g/min. After the coating process the sprayed samples were dried at room temperature. In order to generate a dense-coated filter system, the cold spray coated filters were thermally treated at 1400 °C in reducing atmosphere. For coating the AC filters using a thermal spray technique, a flame spray unit was equipped with alumina-flexicord which is composed of 99.7 wt.-% Al_2O_3 and 0.3 wt.-% other oxides as impurities. The alumina cord was fed to the flame spray gun and melted by the high combustion temperature of oxygen and acetylene of approx. 3160 °C. After melting, the fluidized alumina was transported by air towards the filter substrate. On impacting on the AC-filter the molten alumina droplets were solidified with an approximate cooling rate of 10^6

K/s. As a result of the high cooling rate high temperature phases were frozen, and through lamination of the droplets dense coatings were formed. Similar to cold spray, five sides of the filter were coated, whereby each side was manually sprayed for 50 s. The instrument setting and parameters of spraying process are displayed in Tab 1. The mass change due to coating the filters was determined. Phase identification of milled powders with a d_{50} of 20 µm based on the coatings was performed by X-ray diffractometry (XRD). In order to evaluate the filtration behavior of alumina-graphite reference filter without and with cold and flame spray coating in direct contact with inclusions containing steel melt, an immersion test was performed in a steel casting simulator. The principle setting of the steel casting simulator has been presented by Dudczig et al. [9]. For each filter sample, approx. 30 kg of steel 18CrNiMo7-6 was melted at 1580 °C under a fully controlled argon atmosphere without any further steel treatment. For each test, a new alumina-spinel crucible was used in order to exclude the effect of corroding refractory crucibles on the inclusions containing in the steel. The prismatic samples were fixed at a special sample holder and immersed into the steel melt for a contact time of 20 seconds while being rotated at 30 rpm. Afterwards, each sample was removed via a double door system and was cooled in a chamber with argon atmosphere to prevent oxidation of carbon-bonded filter substrate. Before and subsequently after immersion of the filters into steel, oxygen content and temperature were determined with a pO_2/T-sensor-system. The surfaces of the filters AC, AC+A CS and AC+A FS before and after immersion into molten steel have been characterized by scanning electron microscopy and digital microscopy.

Tab. 1: Parameters of the flame spray process

Flow of oxygen gas (m^3/h)	3.2
Flow of acetylene gas (m^3/h)	0.8
Flow of air (m^3/h)	28
Gun-to-filter distance (mm)	100
Precursor feed rate (mm/min)	230

RESULTS AND DISCUSSION

Filter coating process

On the one hand, the alumina-graphite filters were coated with alumina slurry via cold spray. After coating, the filters have to be dried and thermally treated in reducing atmosphere. Tab. 2 displays the change in weight during these process steps. After spraying and drying the AC-filter, sample AC+A CS showed a weight increase of 5.8 g, which includes the alumina material as well as additives. After thermal treatment at 1400 °C in reducing atmosphere, the total weight of filter AC+C CS was28.5 g. Since the alumina-graphite filter does not lose any weight during carbonization, the cold spray technique adds a coating with a total weight of about 3.1 g (12 % of the filter weight). After flame spray process, the Al_2O_3-C filter with alumina coating (AC+A FS) weighed 31.5 g, which implies an alumina coating weight of 6.2 g (25 % of the filter weight). In contrast to cold slip spray, an additional thermal treatment is not necessary.

Tab. 2: Weight changes during process steps

Filter	Initial weight (g)	Weight after coating process (g)	Weight after thermal treatment (g)	Weight after immersion test (g)
AC	25.3	-	-	25.2
AC+A CS	25.4	31.2	28.5	36.1
AC+A FS	25.3	31.5	-	36.1

Filter characterization

After the coating process, the properties of the alumina coatings prepared by cold and flame spray were investigated. As the slip for cold spray coating is composed of 35 wt.-% water and additives which both disappear during thermal treatment, the coating exhibits a high porosity of approx. 36 %. In contrast, flame spraying took place with dry powder-based flexicords. However, thermally sprayed layers are known to be anisotropic and have many defects including pores, microcracks, unmolded particles, and isolated large particles. Consequently, the flame spray coating is not completely dense but has a low porosity of 10.8 % and as a result a much lower permeability. By analyzing the surface with aid of digital microscope, shiny carbon is visible at different areas at the top of the Al_2O_3-C reference filter (sample AC) (Fig. 1a and b). At higher magnification, also some fine cracks can be detected on the filter struts (Fig. 1c). The cold sprayed alumina coating (sample AC+A CS) covers the filter substrate very homogenously (Fig. 1d). However, large cracks cross the coating, which are caused by degassing of water and additives as well as by shrinkage during the thermal treatment (Fig. 1e). In comparison to the alumina-graphite filter the cracks are much longer, show a greater width and expose the black colored filter substrate (Fig. 1f). The flame spraying led to a much more irregular and rougher coating on sample AC+A FS (Fig. 1g-i).

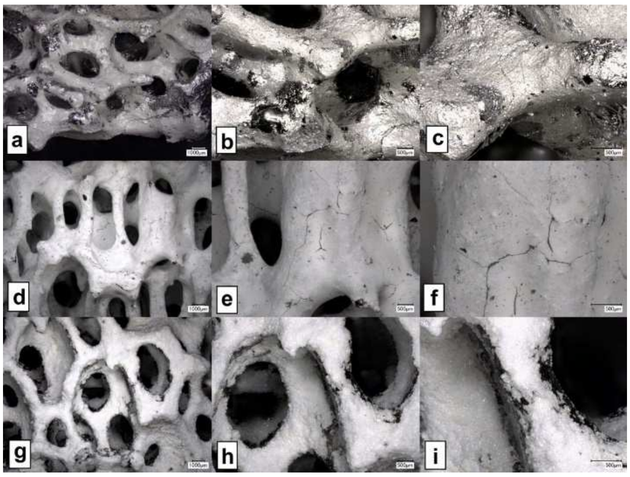

Fig. 1: Condition of filter AC (a-c), AC+A CS (d-f), and AC+A FS (g-i) at 20x, 50x, and 100x magnification

Compared to cold slip spray, the flame spray particles have less fluidity which can be explained by the rapidly cooling of the molten alumina splats after impacting on the substrate. Hence, there is no drifting of particles along the surface of the filter struts. This will lead to a patchy coating which is predominantly present at the top of the struts and filter parts which face to flame spray gun but not at the side and back of the struts, and deeper filter parts which are covered by the top region. Also, the coating thickness has been calculated with aid of digital microscope. The slip spraying process led to average coating thickness of 20 µm. By the flame spraying process, a coating with average thickness of 90 µm was generated on the surface. Both measurements are representative for coating thickness at different spots at the top of the filters. The results of the investigation of the filter surface in SEM can be found in Fig. 2.

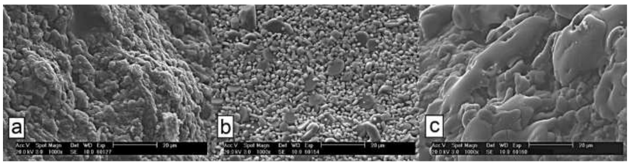

Fig. 2: SEM-image of the surface of filters AC (a), AC+A CS (b) and AC+A FS (c) at 1000x magnification

The surface of the Al_2O_3-C filter AC is very inhomogeneous. There are amorphous carbon-rich areas and fine round alumina particles with maximum particle size of approximately 5 µm detectable. In contrast, the surface of the alumina coated filter

AC+C CS is much more homogenous and round or tabular crystals in different particle classes reaching from 2 to 10 µm can be found. After flame spraying, the typical structure of overlaid molten droplets is visible. At some locations on the surface, the subjacent alumina-graphite structure can be seen. Furthermore, some microcracks cross the droplets.

Fig. 3 displays the X-ray diffraction spectra with corresponding phase evaluation. The Al_2O_3-C filter is composed of rhombohedral corundum (α-Al_2O_3) and graphite (hexagonal carbon). After thermal treatment of 1400 °C in reducing atmosphere, the slip-based cold sprayed coating is completely composed of rhombohedral corundum (α-Al_2O_3). During thermal spraying, the high cooling rates (10^6 K/s) of particles impacting on the substrate cause the formation of unusual amorphous, microcrystalline, metastable phases, or high temperature modifications, which will not normally be found in sintered or cast materials at room temperature. Hence, the diffractogram of the flame sprayed coating shows a typical high amount of amorphous portion, and only a few evaluable peaks. These peaks can be assigned to rhombohedral α-Al_2O_3 and predominantly a metastable cubic γ-Al_2O_3 phase, which shows a slightly deformed elemental cell due to the high cooling rate.

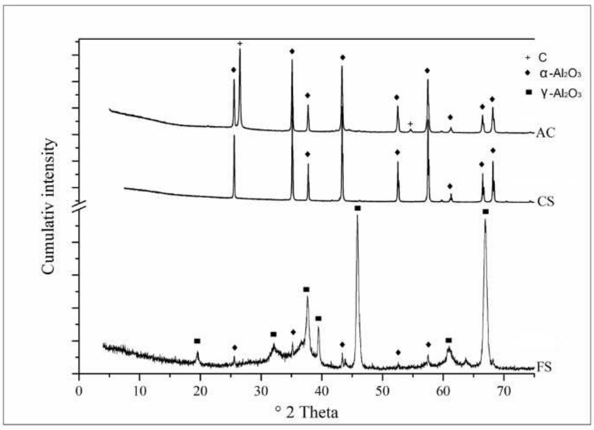

Fig. 3: X-ray diffraction spectra of the filters

Filtration test in steel casting simulator

The steel casting simulator was used to evaluate the interaction of alumina coating applied on an Al_2O_3-C filter with molten steel. No additional steel treatment has been performed in order to investigate the interaction with initial steel inclusions without generating inclusions due to deoxidation effects. Before and after immersion, oxygen and temperature were measured. The testing procedure, as well as the results of the measurements, can be found in Tab. 3. The majority of the nonmetallic inclusions of the steel filtered by the ceramic foam filters are based on oxygen. Thus, decreasing oxygen content is considered to be related to the deposition of inclusions on the filters. The initial oxygen content depends on the steel temperature as well as on the deoxidation agent. Considering the same deoxidizer, the higher the steel temperature, the higher the oxygen content. Due to different initial temperatures, this correlation leads to different oxygen contents before immersion for every single test. However, being in a range of 25 to 35 ppm, the oxygen contents of all three filter tests before immersion are in a narrow range to reliably evaluate the change of oxygen content due to immersion. The Al_2O_3-C filter was immersed into a steel melt with 1591 °C and 34.7 ppm O_2. During immersion, both the temperature and the oxygen content stay in the same level, indicating only slight deposition of oxygen-based inclusions on the filter struts. Filter sample AC+A CS was immersed into a steel melt with 1583 °C and 33.6 ppm oxygen. After immersion, a lower temperature of 1576 °C and lower oxygen content of 30.9 ppm were detected. However, as the oxygen content decrease can be associated with lower temperature, it cannot be stated or quantified whether the filter and its coating plays a role in the decrease of oxygen. Before immersion of the flame spray coated filter sample AC+A FS, a comparatively low temperature of 1574 °C and oxygen content of 25.8 ppm were measured. After immersion, a higher temperature of 1579 °C was detected and the oxygen content remarkably decreases from 25.8 to 17.3 ppm. This oxygen decrease is an obvious evident for interaction of the flame spray coated filter with the steel melt and its inclusions.

Tab. 3: Testing procedure and results of O_2-T-messurement during immersion tests in steel casting simulator

	Filter		
	AC	AC+A CS	AC+A FS
T before immersion (°C)	1591.4	1582.8	1573.5
O_2 before immersion (ppm)	34.7	33.6	25.8
Immersion and rotating (20s, 30 rpm)			
T after immersion (°C)	1592.2	1576.3	1579.4
O_2 after immersion (ppm)	33.4	30.9	17.3

Filter characterization after immersion tests

Fig. 4 displays the lower part of the three filters after contact with steel melt. After immersion into molten steel, the initially black colored Al_2O_3-C filter appears uniformly gray, most likely due to carbothermal reduction (Fig. 4a). The weight of the filter including the steel spherules was 25.2 g, which means a loss of weight of approx. 0.4 % (see Tab. 2). This must be associated with degassing of carbon, which will influence the carbon content and quality of the steel. The color of the alumina coated filters AC+A CS and AC+A FS also convert from white to gray indicating interaction with steel melt (Fig. 4b and c). After contact with the steel melt, both filters weighted 36.1 g. This implies a weight increase of 27 % for the cold-coated filter AC+A CS, which includes the steel spherules and trapped inclusions on the filter struts surface. The weight of the flame sprayed filter AC+A FS increases by 14 %.

Fig. 4: Condition of AC (a), AC+A CS (b) and AC+A FS (c) after immersion test

In addition, the surface of Al_2O_3-C filter, AC, has been investigated by SEM after immersion into molten steel. The investigation reveals a very porous structure composed of alumina, which was formed by burnout of the carbon compound as well as the generation of suboxides. Furthermore, many steel particles are detectable within the microstructure. However, even at high magnification neither a newly formed layer nor depositions of inclusions are detectable. Based on SEM results, with exception of carbothermal reduction of the surface, there seems to be no interaction with inclusions of the steel melt after 20 s contact time at 1580 °C in steel casting simulator. After immersion into molten steel, filter AC+A CS also reveals a porous structure with steel particles. Additionally, many small plate-like crystals are detectable, which are in an initial state of growth. These are trapped particles formed by in situ nucleation of alumina from the aluminum dissolved in the steel [6]. Their formation consumes oxygen, which results in lower oxygen content of the steel melt measured during the immersion test. With higher magnification, numerousness very small particles are detectable, which have the typical shape of endogenous inclusions and adhere to the coating, or on top of the plate-like crystals. Fig. 5 displays a filter strut with an in situ formed layer on its top (marked with white arrow). The in situ formed layer can be amorphous, crystalline (α-Al_2O_3) or a mixture of amorphous and crystalline, which depends on the impurities of the ceramic raw material, impurities in steel, and alloy elements. On top of this in situ formed layer, nanometer sized endogenous inclusions can be found as clusters having a size in range of 1 µm.

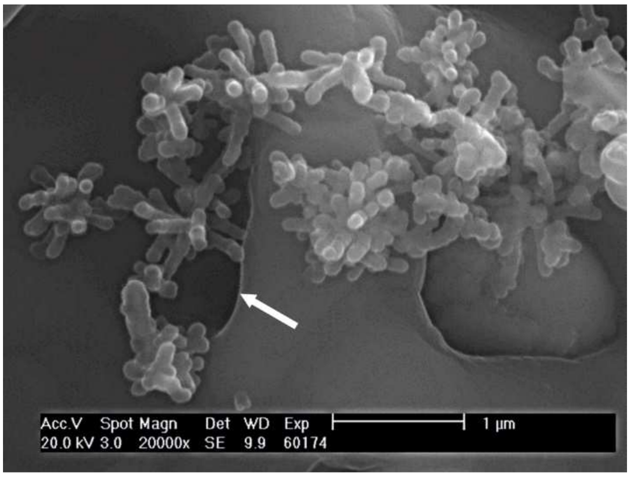

Fig. 5: Inclusions and in situ formed layer

Most of the microstructure of flame sprayed filter AC+A FS is composed of a mixture of irregularly round particles with different grain sizes and the typical plate-like trapped particles. Compared to filter AC+A CS, the microstructure is much denser with less porosity and the plate-like crystals and particles seem to cover nearly the whole flame spray coated filter. The buildup of the comparatively thick new layer by nucleation of dissolved aluminum consumes oxygen, which explains the remarkable decrease of oxygen content of the steel melt during immersion test. Furthermore, the formation of such a dense and thick layer after contact to molten steel illustrates the high reactivity of amorphous and γ-Al_2O_3 phases formed by flame spraying process. On these particles and plate-like crystals, much smaller endogenous inclusions can be found. However, there is no evidence of an in situ formed layer like the one detected at the top of cold spray coated filter AC+A CS. This can be explained by the absence of raw material impurities like SiO_2, Na_2O, and K_2O. During the flame spraying process with the temperature above 3000 °C, these impurities are volatile gases and do not impact at the filter surface leading to an alumina coating with a high purity. Earlier investigations have found a promoting effect of the in situ formed layer on the deposition of inclusions [9]. Furthermore, Poirier et al. states that a higher gaseous transfer will increase alumina buildup [6]. Hence, a porous filter material with many impurities (e.g. cold sprayed alumina coating) will result in higher filtration efficiency by deposition of many impurities. However, the dense and pure flame sprayed alumina coating exhibits a much higher amount of trapped particles on its surface, indicating that the high reactivity of the flame sprayed alumina compensates these differences in structure. There are two main advantages: a much higher filtration efficiency proven by a higher amount of trapped particles and less impairment of the steel melt by fewer interactions of the steel with the alumina-graphite substrate filter due to the dense flame sprayed alumina coating.

CONCLUSIONS

Alumina-graphite filters are an excellent choice for steel casting as they exhibit high creep resistance and provide low weight and thermal mass. During contact with molten steel, Al_2O_3-C filters exhibit intense decarburization, but nearly no deposition of inclusions from the steel melt. The slip sprayed alumina filter needs an additional thermal treatment and interacts with the Al_2O_3-C filter substrate and steel. Consequently, many small plate-like crystals formed by in situ nucleation of alumina from the aluminum dissolved in the steel are detectable. Additionally, due to the presence of impurities, an alumina-rich layer is formed, on which nanometer sized endogenous inclusions can be found. Flame spray coating processes need no additional thermal treatment but generate an inhomogeneous and rough coating, which is predominantly present at the surface of the filter and is composed of metastable γ-Al_2O_3. As it covers the cracks of the alumina-graphite filter substrate, it will be possible to produce even bigger ceramic foam filters with high mechanical strength. After immersion into molten steel, most of the microstructure is composed of irregularly round particles and typical plate-like trapped particles, which cover nearly the whole surface of the flame spray coated filter. The buildup of the new layer accompanied by a remarkable decrease of oxygen content of the steel illustrates the high reactivity of flame sprayed coating. On these particles, endogenous inclusions, but no in situ formed layer, can be found as the flame spray coating contains nearly no impurities. In addition to a much higher filtration efficiency, less impairment of the steel flow due to higher density takes place. Hence, a thermal spray coating is recommended for filtration of cast products with a high demand on cleanliness.

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