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Development of multi-walled carbon nanotubes-based coatings on carbon-bonded alumina filters for steel melt filtration

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Abstract

Ceramic foam filters (CFFs) have been used by steel foundries for several years to remove non-metallic inclusions from the metal castings. In order to improve their filtration efficiency, promising approaches which involve "active" and "reactive" coatings applied on the filters have recently been proposed.

In this work, a new coating system containing multi-walled carbon nanotubes (MWCNTs) is presented. A special water-based dispersing technique for carbon nanotubes was developed. Xanthan gum was used both as a dispersing agent and as a rheology modifier for the spraying slurries. The synthetic coal tar pitch Carbores® P was added as a binder for the carbon nanotubes. The coatings were cold-applied on 10 pores per inch (ppi) carbon-bonded alumina filters previously manufactured via the Schwartzwalder process. After drying, the samples were heat treated at 800 °C. The performance of the coated filters was investigated with the aid of a special steel casting simulator in fully-controlled atmosphere.

Keywords: Carbon nanotube; Alumina; Carbon; Ceramic foam filter

1. Introduction

There exists an increasing pressure on the metal-making and metal-using industry to remove solid and liquid inclusions such as deoxidation products (oxides), sulfides, nitrides, carbides etc. and thereby improve the quality of the produced metal parts. 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 in excessive casting repairs or rejected castings.[1] Ceramic foam filters (CFF) have been used in steel application for several years to remove such inclusions and ensure the requirements of high purity metal castings.[2–4] In particular, carbon-bonded alumina filters offer improved thermal shock performance and increased creep resistance, allowing larger foam filters macrostructures for filtration of large steel casting.

In order to achieve higher filtration efficiency, Aneziris et al.[5–8] have proposed a new approach of surface functionalized filter materials based on "active" and "reactive" coatings. In case of so-called "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.[9] 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.[10]

Nano-scaled materials have been used in numerous technological fields for many years and present nowadays a rapidly growing market in the material science field. In terms of this contribution, new carbon-bonded alumina CFF with cold-applied MWCNTs coatings will be presented. Carbon nanotubes have a unique set of properties that enable them to be considered for a wide scope of possible applications, mainly in suspensions and polymer-based solutions, melts and composites. Their outstanding characteristics include good mechanical properties, namely high tensile strength and elastic modulus coupled with a remarkable flexibility, excellent thermal and electric conductivities, low percolation threshold (loading weight at which a

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sharp drop in resistivity occurs) and high aspect ratios (length to diameter ratio, *L*/*D*). The latter provides the nanotubes with additional advantage over spherical fillers to obtain composites with advanced features. As demonstrated by Peigney et al.,[11] the specific surface area (SSA) values of carbon nanotubes are scattered on a very broad scale, from about 50 m^2/g (for MW nanotubes 35 nm in diameter with 40 nm walls) to 1315 m^2/g (for single-wall nanotubes). Based on these values, any coating made from CNTs can potentially increase the effective surface of a filter and thus its reactivity, especially when the nanotubes have a low number of shells and are homogeneously distributed on the substrate material with their walls exposed. A larger surface area obviously promotes the interaction between the filter and the steel melt. During operation, the majority of the carbon from the nanotubes is expected to be consumed either by the dissolution into the melt or by the reaction with the oxygen from the melt according to the following:

$$C_{(s)} = C_{(diss.)}$$

$$C_{(s)} \text{or} C_{(diss.)} + O_{(diss.)} = CO_{(g)}\uparrow$$

When the second reaction is predominant, less ternary and quaternary inclusions can be expected in the steel products due to less oxygen dissolved in the melt. In a recent work Dudczig et al.[12] have observed that carbon-bonded alumina filter material reacts in situ when immersed in a steel melt, forming gaseous alumina sub-oxides which in turn react with the dissolved oxygen of the steel and create a thin alumina layer (identified as crystalline α-alumina at room temperature) on the contact area with the steel. As a result, sintered fine endogenous inclusions are found in various shapes on this layer. The present work is the first attempt to exploit the high reactivity characteristic of the carbon nanotubes for a steel melt filtration purpose: a thin CNTs-based coating on a carbon-bonded alumina filter could possibly promote and accelerate the aforementioned reactions between the steel melt and the filter material. A faster and more efficient formation of the thin alumina layer could result in a larger entrapment of endogenous inclusions and consequently in cleaner final steel products. Considering that in the experiment conducted by Dudczig a very short (60 s) immersion time was adopted, even a small improvement could have a great impact on the whole filtration process.

Despite their exciting properties, nowadays the effective utilization of nanotubes depends to a large extent on the ability to create aggregation-free homogeneous dispersions and orient CNTs in liquid and melt phases. The nano-scale dimension of CNTs coupled with their surface characteristics turns dispersion into a challenge, since as the surface area of a particle increases, so does the attractive forces between the aggregates. High aspect ratios, combined with high flexibility, increase the possibility of nanotube entanglement and close packing: pristine CNTs tend to assemble into bundles or ropes, which contain hundreds of close-packed nanotubes tightly bound by a van der Waals attraction energy of 500 eV/μm for tube-tube contact.[13] There are two distinct approaches for dispersing carbon nanotubes: the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (non-covalent treatment) or chemically (covalent/ionic treatment). The latter uses surface functionalization of CNTs to improve their chemical compatibility with the target medium, however it is well known that the use of neat acids at high temperatures can introduce structural defects resulting in inferior properties for the tubes. On the contrary, physical adsorption of long chain polymers is particularly attractive because the π system of the graphene sheets is not disturbed. In a typical dispersion procedure, surfactant adsorption is combined with ultrasonication: the role of ultrasonic treatment is to provide high local shear, particularly to the nanotube bundle end. Anionic surfactants such as sodium dodecyl sulfate (SDS) and dodecyl-benzene sodium sulfonate (NaDDBS) have been widely used to limit the agglomeration tendency of CNTs in water due to charge repulsion.[14] It has been shown that polymers containing aromatic groups generally provide good surfactant-tube affinity, thanks to π-stacking interactions of the benzene rings onto the CNT surface. Biopolymers such as gum arabic or gelatin have also been introduced for drug delivery applications, where aromatic surfactants would be toxic. Polysaccharides with a good toxicological profile bring both steric repulsion and better stabilization (as thickeners) of the aqueous dispersions of carbon nanotubes.[15,16] Polaczek et al.[17] reported that complexation by polysaccharides involves, to a certain extent, interactions between the hydrophobic surface of nanotubes and hydrophobic sides of the saccharide units. However, clathration of nanotubes in the polysaccharide matrices seems also to be essential. In the present contribution, MWCNTs were dispersed in water by means of ultrasonication coupled with non-covalent treatment (using a biopolymer), applied to carbon-bonded alumina filters and tested for steel melt filtration.

2. Materials and methods

The raw materials used for the preparation of our coatings were MWCNTs (TNM8, Chengdu Organic Chemicals, Chengdu, China, purity >95%, outer diameter > 50 nm, length = 10–20 μm), and modified coal tar pitch powder (Carbores® P, Rütgers, Castrop-Rauxel, Germany, $d_{90} < 0.2$ mm – used as a binder). The additives were Xanthan powder (Rhodopol, standard 50-mesh – used both as a dispersing and thickening agent), ammonium-lignosulfonate (Otto-Dille, Germany – used as a wetting agent) and Contraspum K 1012 (Zschimmer & Schwarz, Lahnstein, Germany – used as an antifoam agent). The carbon nanotubes were used as received, without further purification.

Xanthan gum (Xan) is a microbial polymer secreted by the *Xanthomonas campestris* with a high molecular weight. It is a branched polysaccharide with weak anionic properties, primarily used as a thickening agent in the food industry and as a stabilizer in cosmetics. Moreover, it has also proved to be effective for the dispersion of CNTs in water, especially when modified with addition of hydrophobic groups.[18] In our work, we took advantage of the shear thinning behavior of Xanthan gum aqueous solutions in order to produce spraying slurries with the appropriate rheological behavior.