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The influence of nanoparticles and functional metallic additions on the thermal shock resistance of carbon bonded alumina refractories

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Abstract

Modern steel casting plants require functional refractory components such as monobloc stoppers, submerged entry nozzles, and ladle shrouds. The functional flow control components in steel casting plants are often made of carbon bonded alumina refractories containing approximately 30% residual carbon after coking. This study investigated the mechanical and thermo-mechanical behavior of different functionalized Al_2O_3–C materials with additions based on alumina nanosheets, carbon nanotubes, semiconductive silicon, and a carbon content reduced to 20%. Furthermore, the curing temperature and the mixing order of the raw materials were altered. By optimizing the curing and mixing conditions of the samples that included all the additives, high residual strengths (with absolute values of up to 14.51 MPa before thermal shock, after the first thermal shock, 12.11 MPa, and after the fifth thermal shock, 13.87 MPa, and a relative values of up to -19.81% and -4.29% respectively) could be recorded after thermal shock treatment.

Keywords: B. Nanomaterial; C. Semiconductor; D. Graphite; D. Alumina; E. Refractory

1. Introduction

With high throughputs and extreme demands on plant materials, modern steel casting plants require high-quality, functional refractory components, such as monobloc stoppers, submerged entry nozzles, and ladle shrouds. High corrosion resistance against both steel and slag melts as well as high thermal shock performance and oxidation resistance at elevated temperatures are typical properties of these functional components. These properties are achieved through specific combinations of materials and specially designed microstructures [1].

One class of refractory materials that fulfills these requirements is the carbon-containing and carbon bonded refractories. The combination of carbon and oxides reduces the material's wettability by slags and molten metals, and also results in a higher thermal shock resistance due to the reduced thermal expansion of the composite and its improved thermal conductivity [3].

The functional flow-control components in steel casting plants are often made of carbon bonded alumina refractories containing approximately 30% residual carbon after coking [2]. One disadvantage due to the flow of molten steel through Al_2O_3–C refractories is the so-called 'carbon pick-up' during steel casting. Deep decarburized steels have a tendency to dissolve the carbon of refractory linings, which has a negative impact on their properties [4–8].

As already mentioned carbon bonded alumina refractories contain 30% residual carbon after coking. With regard to the 'carbon pick-up' the carbon content should be reduced. However, the properties of carbon bonded alumina refractories should be maintained. Previous work has demonstrated that admixture of semiconductive silicon has a positive effect on the properties of refractories. This could be attributed to the property of semiconductive silicon to transfer electrons to the macro-molecules of the carbon-based binding phase [19]. With

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this transfer a higher amount of carbon in the samples after coking has been registered. With this higher carbon content inside the binding phase, resulting in a lower porosity the mechanical properties such as the cold modulus of rupture and thermal shock resistance could be improved [19,20]. Another approach is the use of additives on the nanometer scale [21]. Tamura et al. [22] and Aneziris et al. [3] proposed the use of nanoscale material additions in refractory applications as early as 2003. In the past, the use of nanoscale materials in carbon bonded refractories was hindered by their extremely high cost of production, as well as difficulties in achieving homogenous distributions in the mixtures.

In recent years, the production of nanoscale materials has become increasingly cost effective. Furthermore, a range of developments in process engineering has facilitated the production of greater volumes of nanoscale materials [23]. Further investigations have also shown that the addition of minor amounts of nanoscale materials can improve the performance of the refractories [23–36]. Roungos and Aneziris [1] explored the addition of alumina sheets in combination with carbon nanotubes in Al_2O_3–C materials. Moreover, it has been demonstrated that mechanical and thermo-mechanical properties are improved by the formation of the Al_3CON phase and amorphous whiskers with platelet structures [14,37,38]. This approach has been also investigated for the MgO–C system by Li et al. [39] and Zhu et al. [40].

Another disadvantage of carbon bonded alumina refractories is the oxidation of carbon, resulting in the loss of positive properties. To improve the oxidation resistance of carbon bonded refractories, antioxidants are incorporated in the mixtures. In general, fine metallic powders (Si, Al) in the range of up to 150 μm are used as antioxidants, as well as carbides (SiC, B_4C, Al_4SiC_4, $Al_8B_4C_7$) and boron-containing oxides (fluxes) in the range of up to 100 μm [9–16]. With the addition of Si, for example, the CO (g) of the surrounding atmosphere forms SiO (g). During this reaction, the CO (g) is reduced to C (s) [13]. In a subsequent step, the formed SiO reacts again with the CO (g) to form deposits as thin protective layers of SiO_2 (s) on the graphite surface [14,17]. This reaction causes a volume expansion, which can close the pores of the refractories [9,18]. If boron is used, this effect may take place due to the formation of a glass phase [11,13,16]. Furthermore, a combination of different antioxidants may be used to further improve the performance of the refractories [10,16].

In the present work, the mechanical and thermo-mechanical behavior was investigated for different functionalized Al_2O_3–C materials with additions based on alumina nanosheets, carbon nanotubes, and semiconductive silicon. For this purpose, model compositions with and without alumina grains were investigated. The aim of this contribution was to investigate compositions with excellent mechanical and thermo-mechanical behavior. Another aim was to increase the carbon binder yield after coking in further investigations. A further purpose was to determine the influence of the curing temperature and the mixing order of the raw materials on the properties of carbon bonded alumina refractories.

2. Experimental

For the model experiments without alumina grains, the following raw materials were used: natural graphite with very fine grains (99.50 wt% < 40 μm, d_{50}=8.50–11.00 μm) and with a carbon content of 90–96 wt%; flaked, coarse-grade graphite (95.00 wt% > 71 μm, d_{50}=140 μm) with 87–98 wt% carbon content, both produced by Graphit Kropfmühl AG, Hauzenberg, Germany; and fine metallic silicon powder (Elkem, Oslo, Norway) of high purity (99.50 wt% < 150 μm, d_{50}=17.30 μm). In addition to these raw materials, different nanoscale materials and a silicon semiconductor as listed in Table 1 were used. In all experiments, a liquid phase (PF 7280 FL 01) and a powder phenolic resin (0235 DP), both from Momentive Specialty Chemicals, Iserlohn, Germany, were added as binders. Furthermore, hexamethylenetetramine (Momentive Specialty Chemicals, Iserlohn, Germany) was used as a curing agent.

In the first step, the model compositions without alumina grains were produced to investigate interactions between the binder, the graphite, and the additives. Therefore, the graphite and the novolak powder resin were premixed in a paddle mixer (ToniMix, Toni Technik Baustoffprüfsysteme GmbH, Model 6209) for 3 min. Next, the nanoparticles and the liquid resin were mixed for 3 min. Partial agglomeration of the raw materials occurred during mixing due to the absence of coarse grains. In Table 2, the compositions of the different model mixtures are listed.

Table 1
Special additives (nanoscale materials and semiconductor).

Additives	Producer	Abbreviation	Purity (wt%)	Average particle size			Specific surface area (m^2/g)	Specific resistance (Ohm cm)	Doping
Carbon nanotubes (C)	Timesnano (China)	TN	≥ 95.00	Outer diameter > 50 nm	Inner diameter 5 – 15 nm	Length 10 – 20 μm	> 40.00	–	–
Alumina nanosheets (α-Al_2O_3)	Sawyer (USA)	AS	95.00 – 99.80	10 – 250 nm			9 – 40	–	–
Silicon	Silchem, (Germany)	Si (special) resp. Si1	–	< 64 μm			–	1.20 – 1.30	Phosphorous