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Phase formation in Al_2O_3-C refractories with Al addition

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ABSTRACT

Depending on the recipe and the firing conditions, several non-oxides can be formed in Al_2O_3-C refractories. In this paper, the effect of the purity of the recipe components on the phase formation in Al_2O_3-C refractories with Al addition was investigated. Two test series were sintered from 800 °C to 1600 °C under air embedded in coke breeze. One test series was with brown fused alumina, and the other was with tabular alumina. At temperatures of up to 1200 °C the phase formation was the same for both recipes. For temperatures greater than 1400 °C, the impurities of brown fused alumina enhanced the formation of a polytype, while Al_4O_4C and $Al_{28}O_{21}C_6N_6$ were formed in the other series. The findings explain the occurrence of several non-oxides in disequilibrium at the chosen temperatures. The occurrence of Al_4C_3 was of particular interest due to its low hydration resistance. It was formed at 1200 °C.

1. Introduction

Alumina-carbon (Al_2O_3-C) refractories are widely used in the steel industry, e.g., for stoppers, ladle shrouds or submerged nozzles. The task of these refractory materials is the control of the flow and velocity of the liquid steel and prevention of the steel from oxidation. Carbon-containing refractories have many benefits as poor wettability by liquid slags, good corrosion resistance, or low thermal expansion, but they could suffer from oxidation. To enhance the oxidation resistance, several metals can be added as antioxidants. Metallic Al and Si are economically affordable in many cases and therefore they are a favoured choice. The antioxidants increase the oxidation resistance of the refractories and form in situ carbides and nitrides, thus improving the mechanical and physical properties [1–4].

Zhu et al. reported that an addition of Al as an antioxidant to the mixture leads to the formation of AlN as a ceramic bonding phase. An addition of Si yields SiC, and if Al and Si are used together with a Ni catalyst, then β-SiAlON is formed acting as a bonding phase [1]. A similar observation was reported by Luan et al. but instead of silicon metal, SiO_2 was used as the recipe component [5]. Li et al. also used Ni as a catalyst together with Si and Al to generate β-SiAlON whiskers [6].

Except of AlN, Al_4C_3 can be formed when Al is used as an additive [2,3,5–8]. Shi et al. found out that the Al_4C_3 and AlN formation begins at 800 °C resulting in a decreased porosity and increased cold crushing strength of the material [7]. SiC and Si_3N_4 are usually detected in the materials when only Si is used [1,4–6,8–11].

Despite the large number of studies performed on the phase formation in alumina-carbon refractories with different antioxidants, some uncertainties still remain regarding the phase composition. In particular, these uncertainties relate to the formation of Al_4C_3. The formation of this phase is important as it is not resistant against humidity and could cause disintegration of the refractory material. According to Zhu et al. the addition of only Al as an antioxidant leads to the formation of AlN in the temperature range 1000–1400 °C, and no Al_4C_3 is formed [1]. Khezrabadi et al. observed the formation of both AlN and Al_4C_3 at 1450 °C [3]. According to the investigations of Li et al. the formation of AlN and Al_4C_3 starts at 800 °C and could be found in the material up to 1400 °C [6]. These as yet unclear phase relations motivated the investigations presented in this study.

2. Experimental procedures

Two different mixtures, test series 1 (TS1) and test series 2 (TS2) (Table 1), were used for the investigation of phase formation in the System Al_2O_3-C-Al in the temperature range 800–1600 °C. The starting materials were coarse and fine white fused alumina (Al_2O_3 99.5%, SiO_2 0.15%, Fe_2O_3 0.05%, Na_2O 0.15%), tabular alumina (Al_2O_3 99.5%, SiO_2 0.15%, Fe_2O_3 0.05%, Na_2O 0.12%), brown fused alumina (Al_2O_3 94.5%, SiO_2 1.6%, TiO_2 2.6%, MgO 0.3%, Fe_2O_3 0.2%, CaO 0.4%, $Na_2O + K_2O$ 0.1%), reactive alumina (Al_2O_3 99.5%, SiO_2 0.03%, MgO 0.07%, Fe_2O_3 0.02%, CaO 0.02%, Na_2O 0.08%, $d_{50} = 2.6$ μm, s.s.a. 3 m^2/g) and flake graphite (C 95%, ash 4%). Solid and liquid

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Table 1
Recipes of the two investigated test series (wt%).

Raw material	TS1	TS2
White fused alumina (1–3 mm)	34.0	
White fused alumina (0–0.5 mm)	31.0	
Brown fused alumina < 0.074 mm	22.0	
Tabular alumina (1–3 mm)		34.0
Tabular alumina (0–0.5 mm)		31.0
Tabular alumina < 0.074 mm		22.0
Reactive Al_2O_3	6.0	6.0
Flake graphite	4.0	4.0
Al powder	3.0	3.0
Phenolic resin	+4.0	+4.0

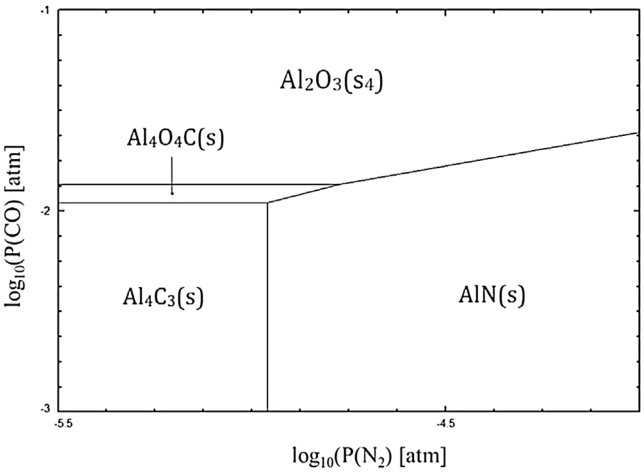

Fig. 1. Predominance area diagram of the system Al-O-C-N at 1000 °C.

phenolic resin was used as a binder. Three wt% aluminium (Al 98.5%, Si < 1.5%, $d_{50} = 45\ \mu m$) was used as an antioxidant in each mixture. The main difference in the two mixtures is the impurity content. In TS1 brown fused alumina was used to determine the influence of impurities on the phase formation. In TS2 pure tabular alumina was used instead of brown fused alumina to minimize the impurity content. Thus, TS1 is considered to be the impure test series, while TS2 is the pure one.

The mixing of the raw materials was performed for 15 min using a compulsory mixer. From these mixtures (TS1 and TS2) cylinders were pressed (height and diameter 50 mm) and cured at 200 °C for 25 h. Afterwards the cylinders were sintered at 800 °C, 1000 °C, 1200 °C, 1400 °C and 1600 °C for 3 h under air embedded in coke breeze. The phase formation was determined by X-ray powder diffraction analysis (XRD) with a Bruker D8-Advanced diffractometer and by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments). The microstructure was investigated using a reflected light microscope (Olympus) and scanning electron microscope (SEM, Carl Zeiss EVO MA15).

Shrinkage and volume expansion were calculated from the weight and size of the samples measured before and after the sintering.

The dynamic Young's modulus (*E*) of the sintered samples was calculated from the ultrasonic velocity and the density. Bulk density (BD) and apparent porosity (AP) were measured by applying Archimedes principle, and the cold crushing strength (CCS) was determined with a uniaxial compression test.

3. Results

3.1. Physical and mechanical properties

The physical and mechanical properties of the tested cylinders are shown in Table 2. The volume change ($\Delta V/V_0$) shows that up to 1000 °C there is a small shrinkage of the samples, whereas at higher temperatures the cylinders expand. The Young's moduli and the CCS are the highest after firing at 1000 °C, and compared the two set of samples TS1 and TS2, the values are always higher for TS2. The density is in all cases close to 3 g/cm^3 and the porosity varies approximately between 14 and 17%. Due to the weak strength of TS2 samples after sintering at 1200 °C it was not possible to measure the physical and mechanical properties of these samples. It was only possible to use a small portion for microscopical investigations.

3.2. Thermodynamic calculations

Thermodynamic calculations in the Al-O-C-N and Al-O-C-N-Si systems were performed using the software FactSage ©. The predominance area diagrams were calculated for 800 °C, 1000 °C, 1200 °C, 1400 °C and 1600 °C.

According to Fig. 1, only AlN or Al_4O_4C should be stable next to alumina. This is the case for all calculated temperatures. The stability regions are shifted to higher N_2 and CO partial pressures with increasing temperature. Under the used conditions the atmosphere should consist of 34.7 vol% CO and 65.3 vol% N_2, and in equilibrium state only alumina should be stable according to the calculations.

The Al-Si-O-C-N System is much more complex. The predominance area diagram calculated for 1400 °C is shown in Fig. 2. Silicon nitride, aluminium- and silicon carbides, as well as oxycarbides, oxynitrides and Sialons are stable.

3.3. Phase formation

The phase formation around the aluminium grains used as antioxidant was analysed with increasing temperature. Fig. 3 shows an overview of the microstructure of the samples from both test series after sintering at 800 °C. The aluminium (white dots) is dispersed in different grain sizes in the matrix of the samples. Also the graphite, visible as long bright lamella, is homogeneously distributed in the microstructure consisting of large and finer alumina grains. In the microstructure there are some pores, which is normal for this type of refractory material. The crystalline phases identified by XRD and EDX resulting from reactions starting around Al are summarized in Table 3. The stoichiometry of the compounds was determined from the measured at% content of the elements.

Table 2
Physical and mechanical properties of TS1 and TS2.

Sintering temperature [°C]	800		1000		1200	1400		1600	
Test series	TS1	TS2	TS1	TS2	TS1	TS1	TS2	TS1	TS2
$\Delta V/V_0$ [%]	−0.4	−0.8	−0.4	−0.4	0.5	1.6	0.4	0.9	0.4
E [GPa]	28.8	44.1	31.8	49.8	24.2	20.6	25.4	21.7	34.3
BD [g/cm^3]	3.0	2.9	3.1	3.0	3.1	3.1	3.0	3.1	3.0
AP [%]	14.6	13.8	14.8	13.7	16.0	15.9	16.6	16.7	16.9
CCS [MPa]	32.6	58.7	54.3	86.7	38.1	47.2	68.8	41.8	60.1

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