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Corrosion resistant sialon–based refractories for applications in the aluminium industry

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Abstract

This papers describes manufacturing the sialon–based ceramics for the modern application in aluminium industry. Sialon based ceramics is characterized by excellent mechanical properties in high temperatures, good corrosion and thermal shock resistance, and low wettability, thus, the sialon material is an ideal candidate for a long term liquid aluminium contact. In the presented method, the relatively cheap and commonly available components, i.e. fine Si and Al_2O_3 powders, were used to obtain reaction bonded materials. The specimens were examined for the phase composition and dimension stability after heating in flowing nitrogen. The corrosion resistance test in liquid aluminium and the test of wettability after sintering were performed. The microstructure of contact surface was examined by the SEM/EDS method. The application of the studied refractories in a horizontal continuous aluminium casting line is planned.

Keywords: Sialon ceramics, Liquid aluminium, Corrosion, Refractories

ODPORNE NA KOROZJĘ SIALONOWE MATERIAŁY OGNIOTRWAŁE DO ZASTOSOWAŃ W PRZEMYŚLE ALUMINIOWYM

W pracy opisano sposób wytwarzania ceramiki sialonowej przeznaczonej do nowoczesnych zastosowań w przemyśle aluminiowym. Ceramika sialonowa charakteryzuje się doskonałymi właściwościami w wysokich temperaturach, dobrą odpornością na korozję i na wstrząsy cieplne oraz niską zwilżalnością, w związku z czym, materiał sialonowy jest idealnym kandydatem w przypadku długotrwałego kontaktu z ciekłym aluminium. W prezentowanej metodzie, wykorzystano względnie tanie i powszechnie dostępne składniki, tj. proszki Si i Al_2O_3, w celu otrzymania reakcyjnie wiązanego materiału. Skład fazowy i stabilność wymiarów badano w przypadku próbek wygrzanych w przepływie azotu. Po spiekaniu przeprowadzono test odporności na korozję w ciekłym aluminium i test zwilżalności. Mikrostrukturę powierzchni kontaktu zbadano za pomocą metody SEM/EDS. Planuje się wykorzystanie badanych materiałów ogniotrwałych w poziomej linii ciągłego odlewania aluminium.

Słowa kluczowe: ceramika sialonowa, ciekłe aluminium, korozja, materiały ogniotrwałe

Introduction

During the last two centuries, the consumption of aluminium was increased from 91 to 36 000 000 tons. It can be said, that aluminium is a leader of the non-ferrous metals group. Main consumers of aluminium products are automotive industry, building industry, and electronics. Development and importance of aluminium origin from its own properties: low density, good atmospheric corrosion resistance, excellent capability to mechanical treatment, moderate price, easy availability in natural resources (~7,5% in the earth shell) and recycling facility. But the most important problem in aluminium products manufacturing origins from low corrosion resistance of refractories in a contact with liquid metal, because aluminium shows a very high chemical reactivity and wettability of most refractories. In contact with molten aluminium, the refractory must resist aluminium penetration, chemical reaction, mechanical abuse, thermal spalling and attack of fluxes. Sialon-based refractories can be a solution, as their low wettability by liquid aluminium was reported earlier [1-2]. Sialon ceramics, based on the solid solution of AlN and Al_2O_3 in β-Si_3N_4, shows excellent corrosion resistance to molten steel [3], slag and aluminium [4], but for application in modern aluminium continuous casting systems, the refractories for feed tubes must meet additionally the following requirements: i) porosity must be in the micrometer range, ii) low surface roughness, and iii) low dimension tolerance together with low production costs are essential. Those problems were solved by the usage of reaction sintering/nitridation of silicon-alumina mixtures and thorough homogenisation of slurries containing the powders with opposite particle surface properties. Nitridation of the silicon compacts leads to the volume expansion and provides dimension stability after the heat treatment process [5-6]. On the other hand, stability of the acidic silicon particles and basic alumina particles in the polar environment can be achieved by addition of the relevant surfactant. The resultant homogeneity and deagglomeration of the slurry will affect particles packing, microporosity and deliver low surface roughness of the final product [7]. The paper describes preparation of the specimens, their properties after sintering and the results of the corrosion test.

Experimental

Two types of batches were prepared, which contain sialon precursors (Tab. 2) for the reaction sintering in the nitrogen flow. According to the Si-Al-O-N system, the final phase

composition should fall into the β-sialon : O'-sialon region. Alumina was introduced in a form of fine alumina (Martoxid MR70) or kaolinite (OK). Silicon (Aldrich 99.99% Si) was used. The composition of the batches is given in Table 1.

Table 1 Composition of sialon precursors as batched.
Tabela 1. Skład prekursorów sialonu w partiach

Specimen	Si [wt%]	Al_2O_3 [wt%]	Kaolinite, [wt%]
A	60	-	40
B	35	65	-

The silicon powder was milled in an attrition mill (Union Process Atritor STD 1) with silicon nitride balls (5 mm diameter) for 4 hrs in isopropyl alcohol. Subsequent mixing of the components was performed in the environment of liquid 2-butanone (MEK)/ethanol with addition of 4 wt% of triethyl phosphate as a dispersant. Homogenisations of the slurry was completed with the aid of ultrasonification for 1 hr (Sonlfier W-450D) and followed by mixing on a roller bench for 48 hrs. The dried powder was then shaped by uniaxial pressing under a pressure of 30 MPa to 20 mm diameter tablets and/or into a form of 50 mm diameter crucible (Fig.1). Subsequently, the specimens (tablets or crucibles) were hold for 1-4 hours at a temperature of 500°C in air in order to remove the organic additives.

Sintering and nitridation was performed in the Thermal Technology graphite furnace in the nitrogen flow. The specimens were placed in a BN crucible with a powder bed of BN+Si_3N_4. The process of nitridation was performed in two steps, i.e. at 1250°C and 1500°C. Each step lasted for 2 hrs. The rate of heating between the steps was 10°C/min. The first step of nitridation was below the silicon melting temperature and was designed to complete the reaction between silicon and nitrogen, whereas the next step, above the silicon melting point, was prepared for the solid state reactions between the as-formed silicon nitride and alumina or kaolinite.

The specimens were measured (diameter and height) and weighed out in a green state and after nitridation/sintering. The Archimedes' method was applied to measure

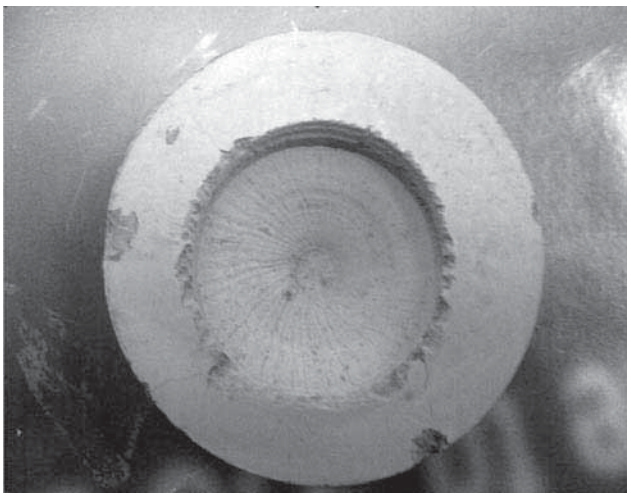


Fig. 1. Green body of the B material-based crucible (Si+Al_2O_3).
Rys. 1. Surowy tygiel (Si+Al_2O_3) wykonany z materiału B.

density and porosity of the sintered bodies. The sintered specimens were cut, and then XRD studies were performed on the exposed surface. The microstructure of the resultant specimens was examined by SEM (Hitachi S-4200).

The static corrosion test was performed in an electric furnace over the melting temperature of aluminium at a temperature of 800°C for 150 hrs in air. Chemical composition of aluminium was ~99% pure. The sample was immersed in liquid metal. After completion of the corrosion test, the specimens were cooled down and cut. The exposed surface was observed by SEM.

Results and discussion

Thermal treatment of the A material in nitrogen resulted in many cracks and metallic inclusions on the surface. The XRD analysis showed only products of the silicon oxidation reaction, only traces of β-sialon were present and core-shell structure was visible in the cross-section of the specimens. Thus the non-reacted silicon must have been left after

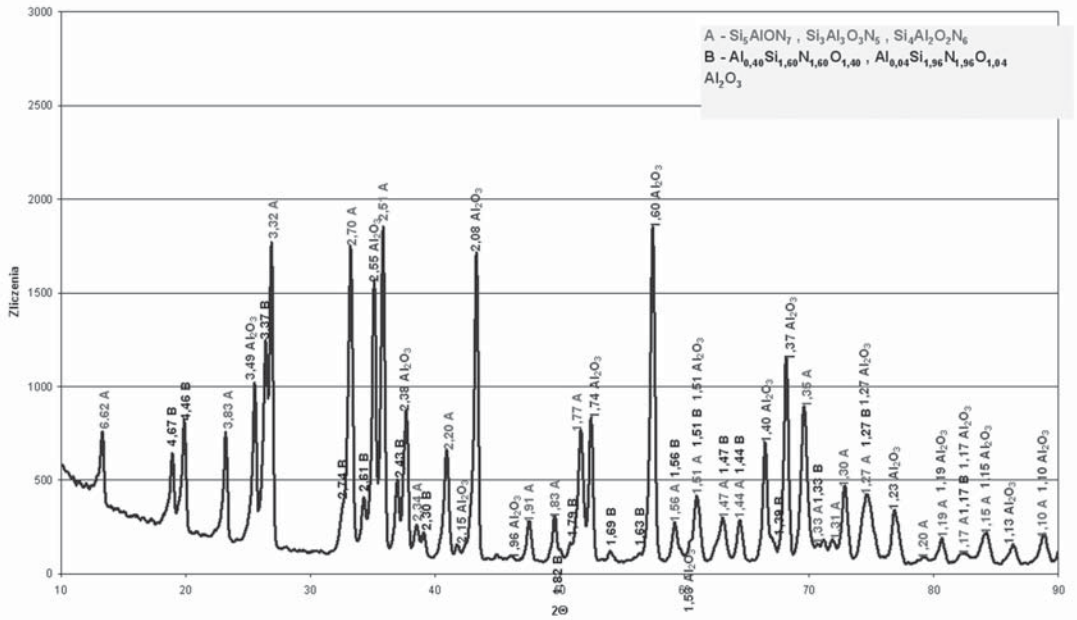


Fig. 2. XRD results of B material after heat treatment in nitrogen.
Rys. 2. Wyniki XRD w przypadku materiału B po obróbce cieplnej w azocie.

completing the reaction at 1250°C and rising temperature over the silicon melting temperature damaged the material. Obviously, the reaction time was too short to complete nitridation of 60 wt% of silicon in the specimen.

In contrary, the results of XRD analysis of the B material (Fig. 2) showed β-sialon (capital A), α-Al_2O_3 and O'-sialon (silicon oxynitride; capital B) as the main phases. Moreover, 33 wt% mass gain was accompanied by good dimension stability after heat treatment; a mean change of dimension was 1,5-2%.

Corrosion test

The specimen (material B) after corrosion test can be seen in Fig. 3.

After cooling, a thin layer of aluminium was found on the specimen surface, but its adhesion to the surface was low and was easily removed by hand. The exposed surface of the specimen was examined by SEM and EDS; the cross-section of the corroded specimen was also observed. The results are shown in Fig. 4.

No metallic aluminium was found inside the specimen, and any visible corroded area was observed. The results of SEM/EDS studies in the micro-areas showed some shift of aluminium content from the specimen surface into its interior, parallel with the silicon content changes. As less aluminium content was observed on the surface exposed to contact with molten aluminium, accompanied by enrichment of silicon, we think that some kind of Al ↔Si replacement reaction could occur during the corrosion test, and those were the only traces of the corrosion reaction.

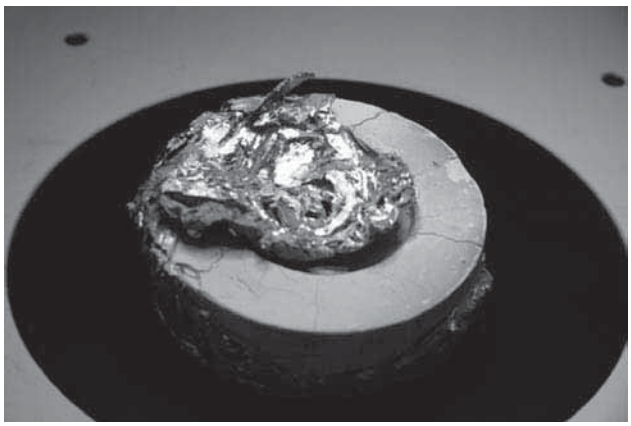
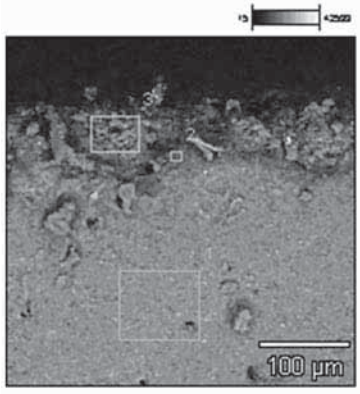


Fig. 3. Material B (crucible) after the corrosion test.
Rys. 3. Tygiel wykonany z materiału B po teście korozyjnym.

EDS analysis showed the presence of other elements in the specimen: Mg, Na, K, probably originated from liquid aluminium. Quantity of this contaminants increased in direction of the specimen interior and it cannot be excluded that this was an effect of the corrosion reaction.

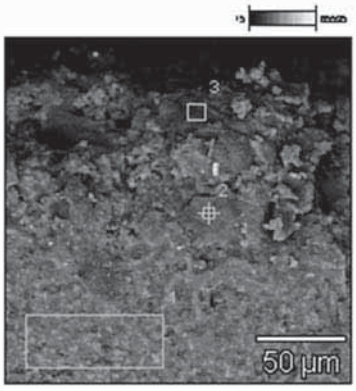
Summary

Silicon-alumina material was successfully shaped and nitrided to β-sialon-O'-sialon-alumina refractory material with low porosity and perfect dimension stability. Linear dimension changes were below 1.5% after sintering. The resultant material showed excellent resistance in contact with molten aluminium after a long exposure time (150 hrs). No corroded areas or aluminium infiltration was observed. The only traces of corrosion test were found as the gradual shift of aluminium from the surface to the specimen interior.



Area	1	2	3
Na-K			1,74
Mg-K	4,57	3,14	3,01
Al-K	38,50	31,82	24,23
Si-K	56,07	63,94	70,28
Ca-K	0,86	1,10	0,74

Accelerating Voltage 25.0 kV;
Magnification: 250



Area	1	2	3
Na-K	1,08		2,23
Mg-K	5,33	7,89	5,87
Al-K	37,26	31,95	20,75
Si-K	55,23	56,73	57,70
P-K			10,37
K-K		1,48	1,44
Ca-K	0,68	1,95	1,64
Ti-K	0,42		

Accelerating Voltage 25.0 kV;
Magnification: 500

Fig. 4. Results of the SEM/EDS analysis (At%) in indicated areas of the cross-section of the B specimen.
Rys. 4. Wyniki analizy SEM/EDS (% at) we wskazanych obszarach przekroju poprzecznego próbki B.

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