The Binding of non-cement refractory castables using the technology of in-situ sol-gel formation

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Abstract

In recent years, silica sol solutions have been increasingly used as cement-free binders in refractory unshaped products. The silica sol solutions are aqueous colloidal dispersions of nanoscale amorphous SiO_2 particles. Compared to conventional high alumina cement-bonded concretes, the silica sol-bonded products are characterized by good alkali and acid resistance. The main advantage, however, is that no calcium aluminate hydrate phases are formed during the setting process and thus these concretes can be heated much faster.

A major disadvantage of silica fume solutions is that they must be stored in separate containers, protected from frost and light. To avoid this, a new system in which the silica sol formation takes place "in-situ" in the refractory matrix is introduced. For this purpose, a microscale amorphous SiO_2 powder is mixed directly into the refractory mass. By adding water, the silica sol formation is generated within the matrix. This eliminates many of the major disadvantages of using aqueous silica sol solutions. The addition of < 1.0 % of this binder leads to good green strengths of the refractory castable. To compare the binding of cement-free and cement-containing refractories, the physical and chemical properties of a nearly pure alumina product was tested. For this purpose, all tests were carried out on the cement containing products and their non-cement counterparts bonded by liquid sol-gel or by the in-situ sol-gel formation. Furthermore, an example of application will be given proving the efficiency of the in-situ sol-gel technique for practical use.

Introduction

The most common binding system for unshaped refractories is based on calcium-aluminate-cement (CAC) which involves the formation of low melting phases like for example anorthite during firing [1, 2]. Therefore, a reduction of the CAC content is desirable. To achieve this, various alternative binding systems like the gel bindings were investigated in the past [3, 4]. The technique of gel binding is known since the 1990's and is mostly used in ultra-low cement castables (ULCC) and no-cement castables (NCC) [3, 5]. Instead of gaining the green strength by the hydration of CACs forming calcium alumina hydrates in sol-gel bonded systems the strength is achieved by creating a 3D-network by polymerization of amorphous silica particles immersed in water. Commonly a dispersion of SiO_2 in water is used as sol-gel for casting. This leads to lower green strength after drying [6]. After firing at temperatures above 900 °C, however, the strength of sol-gel bonded castables is higher than the one observed in cement-containing bonding systems [3]. Due to the absence of calcium hydrate phases during setting, the refractory castable can be heated at a higher rate [7, 8]. Furthermore, sol-bonded products show a higher alkali and acid resistance compared to cement bonded ones. The downside of using sol-gel as binder is its complex storing in separate canisters for liquids. To avoid the difficult storage of the silica fume solutions due to its vulnerability to light and frost, < 1 % microscale amorphous silica powder can be added to the mixture [9]. By casting it with water, a process of "in-situ sol-gel" formation occurs and leads to a sufficiently high green strength. This binding system can be applied to any kind of raw material-based refractory mix, and due to the low addition of silica powder, results in a pure chemical composition that does not impact the melting temperature of the refractory.

Methods

A high alumina thixotropic ULCC product was used as reference and modified to a NCC variant using a liquid sol-gel (NCC-L) and to another NCC variant by adding a microscale amorphous silica powder (NCC-P). After hydration, the microscale amorphous SiO_2 powder in combination with fine MgO as a gelling agent accounted for a binding in an otherwise pure Al_2O_3 system (Table 1). Consequently, the SiO_2 and MgO content is slightly raised, and the CaO content is lowered compared to the ULCC. In case of the NCC-L, a sol-gel with the composition of 30 % SiO_2 and 70 % water was added to the modified base recipe (Table 1). Compared to the NCC-L, the SiO_2 content in the NCC-P is 1.5 % lower, which leads to a SiO_2 content of below 1.0 % in the NCC-P (Table 2).

Table 1: Composition of the tested products

	Raw material	Mixing agent
ULCC	alumina, CAC (0.45 %)	4.5 % water
NCC -P	alumina, fine MgO, fine SiO2	5.4 % water
NCC-L	alumina	7.0 % sol-gel (30 % silica, 70 % water)

Three bars and one cylinder were casted for each recipe. These were dried at room temperature as well as at 110 °C for 24 h, respectively. Afterwards two of the samples were burned at temperatures of 1000 °C and 1500 °C. All three bars of each product were used to measure the PLC (permanent linear change), the CCS and CMOR by using a standard test machine from Form+Test.

Pieces of each bar were pulverized and investigated via X-ray diffraction (XRD) measurements. For this purpose, a PANalytical X'Pert^3 diffractometer with a Cu K_α X-ray tube was used.

For the refractory under load measurement, the casted cylinders were pre-fired at 1000°C for 24 h and polished on the surface. The measurement was performed with a machine from Netzsch Gerätebau GmbH with a uniaxial pressure of 0,2 N/mm^2 during constant heating.

Table 2:Chemical composition of the tested high alumina product with CAC, sol-gel and in-situ sol-gel after drying (110 °C, 24 h).

Oxide	ULCC	NCC-P	NCC-L
Al2O3	99.0	98.7	97.4
SiO2	0.0	0.4	1.9
CaO	0.4	0.0	0.0
Na2O	0.3	0.4	0.4
MgO	0.1	0.4	0.1

Table 3: Phase compositions of the samples ULCC, NCC-P and NCC-L after firing at different temperatures.

Binding system	**Temp / °C**	**corundum**	**β-alumina**	**hibonite**	**mullite**	**others**
ULCC	110	95.4	3.8	-	-	0.7
	1000	94.3	4.4	-	-	1.3
	1500	90.5	3.9	5.4	-	0.2
NCC-P	110	96.0	3.8	-	-	0.1
	1000	96.4	3.2	-	-	0.2
	1500	97.8	0.8	-	-	1.3
NCC-L	110	96.0	3.7	-	-	0.2
	1000	96.0	3.6	-	-	0.2
	1500	97.7	0.5	-	1.4	0.2

Results and discussion

According to the X-ray diffraction patterns, the samples ULCC, NCC-P and NCC-L consist of 95.4 % - 96.0 % corundum and 3.7 % - 3.8 % β-alumina. After firing, the amount of corundum in the ULCC decreases from 95 % to 91 % and increases from 96 % to 98 % in the cement-free samples NCC-P and NCC-L. The latter is accompanied with the decrease of β-alumina to nearly 0 %. Beside this, the ULCC formed CA_6 (hibonite) consuming the cement phases at 1500 °C whereas in the NCC-L the relatively high amount of SiO_2 leads to the formation of mullite. None of these phases can be observed in significant amounts in the sample NCC-P due to the high purity of the system (Table 3). In contrast to that, a small amount of SiO_2 and $MgAl_2O_4$ (spinel) can be found due to the use of MgO as a gelling agent.

Due to the formation of calcium aluminate hydrate phases, the green strength of the ULCC is higher than that of the NCCs. Compared to the NCC-P, the green strength of the NCC-L is slightly higher. This is probably caused by the higher initial amount of silanol groups (Si-O-H) in the sol-gel compared to the powder (Figure 1, Figure 2).

After firing at 1000 °C, the CCS and CMOR of the cement-containing ULCC become lower than the ones of the NCCs, which is related to the decomposition of the CAH phases. The NCC-L has a significantly higher SiO_2 content compared to the NCC-P and thus the sintering temperature is lowered due to the lower melting point. For the same reason, the CCS and CMOR of the NCC-L are higher than the ones of the NCC-P (Figure 1, Figure 2).

With further increase of the temperature to 1500 °C, the CCS and the CMOR of the ULCC increases due to the formation of hibonite and the CCS overcomes those of the NCCs. In contrast to that, no large increase in the strength of the NCC-L can be observed (Figure 1, Figure 2). This can be also related to the high SiO_2 content, which not only lowers the sintering temperature, but also decreases the melting point. Without the high amount of SiO_2, melting occurs at a higher temperature. Thus, the strength of the NCC-P increases due to the sintering of the nearly pure Al_2O_3. This effect leads to a higher CMOR of the NCC-P compared to the NCC-L and ULCC (Figure 1, Figure 2).

The increase in the strength of the ULCC at 1500 °C is also related to a volume expansion at 1400 °C measured by the refractory under load test (Figure 3). This expansion might be related to the formation of hibonite. The NCC-L shows a lower refractoriness compared to the NCC-P (Figure 3). This can also be explained by the relatively high content of SiO_2 of approx. 2 % in the NCC-L compared to the NCC-P. Therefore, a suitable strength and refractoriness can be achieved in a nearly pure Al_2O_3 system with a SiO_2 content of < 1 %.

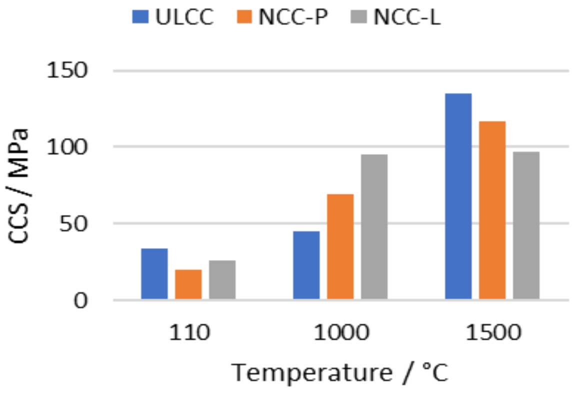

Figure 1: Cold crushing Strength (CCS) of the tested ULCC, NCC-P and NCC-L castable.

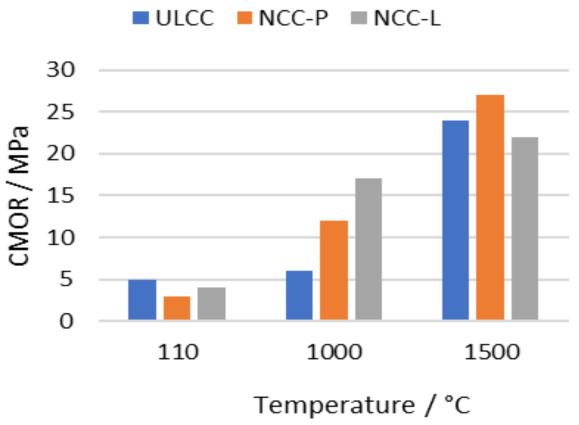

Figure 2: Cold modulus of rupture (CMOR) of the tested ULCC, NCC-P and NCC-L castable.

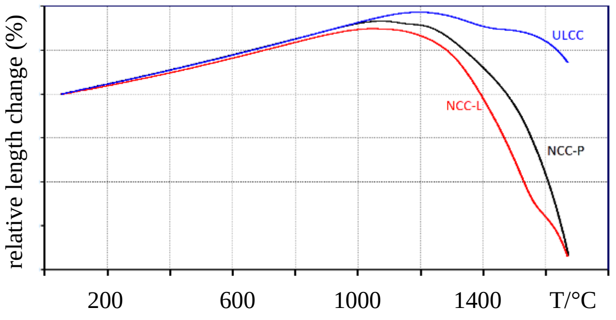

Figure 3: Refractory under load measurement of the analyzed ULCC and the NCC variants with sol-gel and the in-situ sol-gel components.

Apart from productions on a laboratory scale, the product based on the in-situ sol-gel binding has been used for casting well blocks in different shapes and dimensions, ranging from 370 mm to 470 mm in height and 360 mm in wide with a cylindrical hole with a diameter ranging from 118 mm to 199 mm (Figure 4). After casting and drying for 24 hours, the NCC-P showed sufficient green strength for demolding. In its application the NCC-P was used with a durability of 52 to 57 heating cycles at a plant site, which is comparable to the performance of spinel-containing alumina products.

Apart from this, the in-situ sol-gel binding system offers the advantages of using solely water for casting. Thus, the installation procedure is comparable to castables with a cement-based binding system. If SiO_2 is added as a powder and not as liquid sol-gel, the binder is already included in the dry-mixture and no temperaturecontrolled storage of supplementary canisters is required. This saves storage space, reduces energy costs and simplifies the transport.

Furthermore, this binding system can be adapted to any products based on MgO, SiO_2 or Al_2O_3. This includes qualities from chamotte to high alumina raw materials. Even SiC can be added to the system. Further investigations of the in-situ sol-gel bindings system and adaptations to different applications are ongoing and will be discussed in the future.

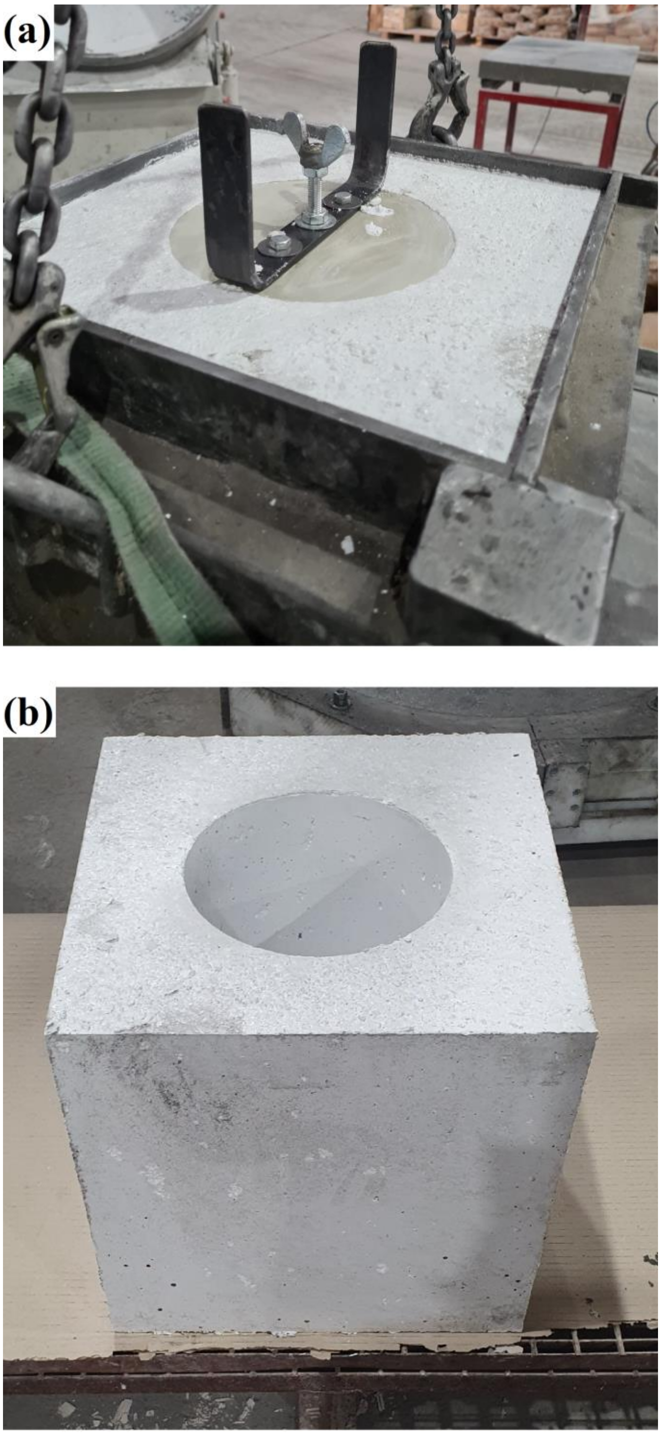

Figure 4: Well block casted from NCC-P mass (a), NCC-P well block after demolding (b)

Conclusions

Besides the conventional binding system based on calcium-aluminate-cements, sol-gel can be used as an alternative approach. Disadvantages associated with the liquid sol-gel can be avoided by mixing a microscale silica powder in the dry-mixture initiating an in-situ formation of the sol-gel by adding water to the product. Compared to the liquid sol-gel, a significantly smaller SiO_2 amount of < 1.0 % is already sufficient to establish an adequate green strength through the silica powder addition. Due to the lower SiO_2 content, the number and the total amount of low-melting phases is diminished leading to higher refractoriness of the in-situ sol-gel bonded sample in a nearly pure Al_2O_3 system.

Based on the service live of the in-situ sol-gel bonded well blocks, the addition of the microscale silica is suitable for the intended application and thus can be used as an alternative to cement. In contrast to the use of the liquid sol-gel binder, the dry-mixture containing the microscale amorphous SiO_2 powder only needs water for casting, making the installation practice comparable to conventional cement-containing products. This delivers an “all-in-bag” solution for cement-free castables.

References

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