

Investigation of properties of boehmitic sol coated graphite added alumina-low cement castables

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In this study, benefiting from the low wettability of graphite, various amounts were added to low cement alumina castables to investigate the resistance of refractories to slag corrosion. For this purpose, typically flake graphite was coated with alumina by a sol-gel method and then added to a mixture of the refractory in various amounts. After the physicochemical investigation, steel ladle slag with a basicity ratio of 2.29 was charged into the crucibles which were prepared according to DIN 51069 standard. After the heat treatment, samples were cut vertically for investigation. For macroscopic analysis, images taken from the slag-refractory surfaces were digitized and subjected to image analyses to investigate the penetration of the slag. Microscopic analyses were carried out with SEM-EDS to determine the elemental dispersion at the refractory-slag interaction zone. Experimental results indicate that the alumina coated graphite addition give improved slag corrosion resistance of alumina castables.

Key words: Sol-Gel process, Al₂O₃-graphite, low cement castable refractory (LCC), mechanical properties, slag-refractory corrosion.

Introduction

Due to its features of non-wettability in contact with liquid slag and liquid metal, it is known that graphite is used in refractories such as magnesia bricks. Using this feature of graphite in applications of castable refractories is desired, yet technical problems are encountered. These difficulties are encountered especially during the mixture of the refractory blend with water. More water needs to be added to the system in order to give the concrete mixture good viscosity because the graphite is non-wettable and a hydrophobic material. More water increases the amount of porosity in the structure of the refractory concrete following drying and firing operations. In order to improve the features of the graphite, a sol-gel method has been used [1-9].

In this study, resistance against a steel slag was examined by producing graphite added alumina castable refractories by a sol-gel method.

Experimental Procedure

Preparation of alumina coated graphite containing low cement castables (LCC's).

For the purpose of producing alumina coated graphite; 650 ml distilled water was heated up to 90 °C and after adding 50 g aluminum isopropoxide (AIP), 26 ml 10%HCl was added to the solution in order to adjust its pH to

2,3 and after mixing the solution for 1 hour, boehmitic sol was produced. By mixing the resulting transparent solution with 400 g layered graphite for 15 minutes and wetting the graphite surfaces, they were given a gel-like form. The natural graphite raw material originating from China contains 95 wt% carbon with a granule size of < 200 μm. The graphite gel coated with the boehmitic sol was kept in a drying oven for 8 hours at 120 °C. The resulting graphite coated with alumina was heated at a heating rate of 2 K/minute up to 550 °C where it was kept for 3 hours [5, 9].

The basic raw materials used in the low-cement castable (LCC) refractory samples include Almasis products containing large - flat alumina crystals; tabular alumina at a quality level of T60, reactive alumina at a quality level of A 1000 SG, micro silica, hydratable alumina and CA - 14 W quality calcium aluminate cement as binder and layered graphite raw materials coated with alumina using a sol-gel method.

The particle size distribution and chemical composition of samples are given in Table 1. *AG0* had no graphite addition; *ACG3*, *ACG6* and *ACG9* respectively contained 3,6 and 9 wt% alumina coated graphite which was produced by a sol-gel method and added to alumina-LCC refractories.

The samples that were first mixed in dry form in a Hobart type mechanical mixer. Then water was added into the mixture according to the ratios specified in the Table 1 and mixing was carried on for 5 minutes more. The LCC cement mortar was cast into 50 mm³ metal moulds, fixed to a vibration table [10, 11]. The cement was kept at room temperature and was allowed to turn into concrete. Then, it was kept in a drying oven for 24 hours at 105 °C. The LCC samples were heated at 10 K/minute

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Table 1. Particle size distribution and chemical composition of LCC refractory samples.

Rawmaterials	Particle size distribution	AG0	ACG3	ACG6	ACG9
		(wt.%)			
	1-5 mm	45	45	45	45
Tabular alumina	0.2-1 mm	19	16	13	10
	0-0.2 mm	11	11	11	11
Reactiv alumina	0-0.02 mm	13	13	13	13
Hydratable alumina	-	5	5	5	5
Micro silica	0-0.06 mm	5	5	5	5
Cement	0-0.045 mm	2	2	2	2
Alumina coated graphite	< 200 mm	0	3	6	9
Water	---	5.4	6.6	7.9	10.0

Table 2. Chemical compositions of LCC samples

wt.%	AG0	ACG3	ACG6	ACG9
Al ₂ O ₃	93.50	90.50	87.50	84.50
C	0.00	0.00	0.00	0.00
C + Al ₂ O ₃	0.00	3.00	6.00	9.00
SiO ₂	4.83	4.83	4.83	4.83
MgO	0.03	0.03	0.03	0.03
CaO	0.64	0.64	0.64	0.64
Fe ₂ O ₃	0.01	0.01	0.01	0.01
Na ₂ O + K ₂ O	0.40	0.40	0.40	0.40

speed to 1600 °C in a SFL-HTCF 940A (UK) make laboratory oven and were kept at temperature for 4 hours and were thus sintered. The chemical compositions of LCC samples are shown in Table 2.

Testing for physical and mechanical properties of LCC's

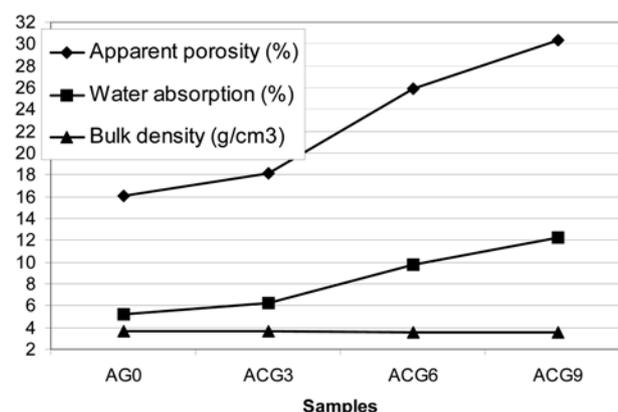
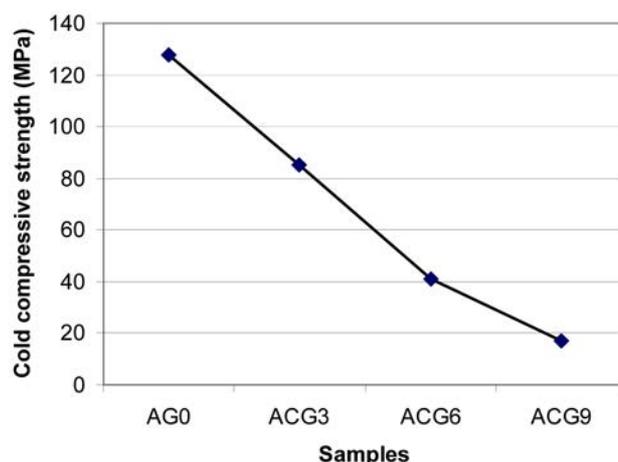
In order to determine the apparent porosity, water absorption and bulk density of samples, experiments were carried out in compliance with the ISO EN 993-1 and 993-2 standards according to Archimedes principle, cold compression tests (CCS) were carried out in compliance with the ISO ENV 1402-6 standard. For the CCS tests, an Atom Teknik (Turkey) pressure device with a loading capacity of 200 tonne max. was used. The physical and mechanical results derived from the experiments are given in Table 3, Figs. 1 and 2.

Corrosion test of LCC's

In order to test the slag resistance of the alumina LCC refractory samples and determine the mechanism of the resulting corrosion, slag-refractory corrosion tests known as the Crucible Method were carried out according to the DIN 51069-2 standard. The slag used was crucible slag supplied from the Erdemir Steel Plant in Turkey. During the experiments, in order to increase the effectiveness of the slag, the slag was granulated in a agate mortar and was sieved through a 100 µm sieve and the granulated slag below the sieve was used. The chemical

Table 3. Physical and mechanical properties of LCC's

Samples	Apparent porosity (%)	Water absorption (%)	Bulk density (g/cm ³)	CCS (MPa)
AG0	16.06	5.23	3.66	128
ACG3	18.11	6.23	3.61	85
ACG6	25.90	9.72	3.59	41
ACG9	30.35	12.22	3.57	17

**Fig. 1.** Physical properties of LCC's.**Fig. 2.** Cold compressive strength properties of LCC's.**Table 4.** The chemical properties of the steel ladle slag (in wt %)

FeO + Fe ₂ O ₃	17.66	P ₂ O ₅	0.617
SiO ₂	14.32	S	0.221
MnO	04.62	Na ₂ O	0.001
Al ₂ O ₃	14.02	K ₂ O	0.107
CaO	32.87	TiO ₂	0.483
MgO	07.01	Cr ₂ O ₃	0.114

composition of the slag is shown in Table 4. The slag has a high basicity and the C/S ratio is 2.29 wt. %.

The castable crucible refractory samples, with steel slag charged into them, were heated in SFL-HTCF 940A model laboratory oven at a heating rate of 10 K/minute up to 1600 °C and were kept at temperature for 2 hours.

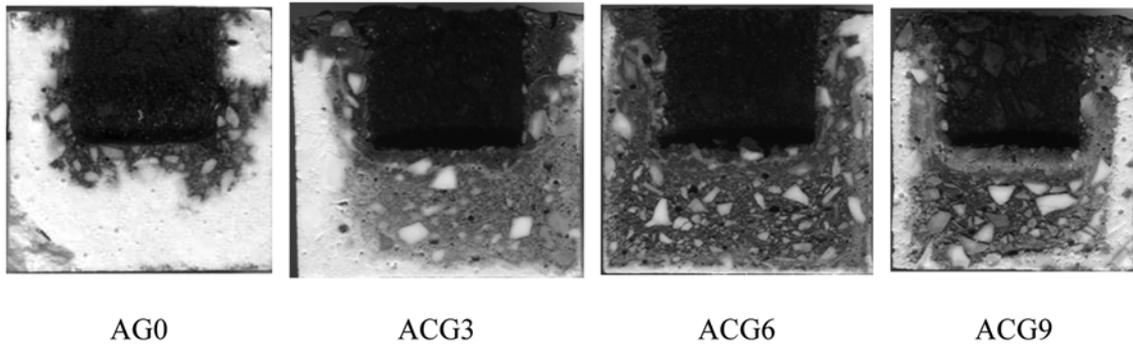


Fig. 3. Photographs of corroded surfaces of LCC's. (edge length of surface = 50 mm.)

Then, the refractory samples which had been corroded by the slag were cut vertically using a hard diamond cutter and the areas where slag had diffused to were uncovered.

Following the initial macroscopic examination, for the purpose of quantitative analysis of the slag diffusion quantities, the slag-refractory corroded surfaces were entered into a computer. In order to do this a HP ScanJet 3970 scanner was used and the slag diffusion surfaces were transferred to the computer (Fig. 3). Then, by using MVH-ImagePCv7 [12] view analysis software, based on the color difference, the slag penetration areas given in Fig. 4 were calculated [13].

After the macroscopic analysis, a microscopic examination was made. In order to consider the corrosive behavior of the steel slag against the refractory at the steel working temperature, the slag diffusion surfaces of the samples were examined by scanning electron microscopy (SEM-Jeol-JSM5910LV, Japan). Also, in order to determine the elemental distribution in this area, an energy dispersive X-ray spectrometer (EDS, IXRF 550i, USA integrated with Jeol) analyses were carried out.

An SEM view of the AG0 sample in the slag interaction area and the EDS analysis of these points in this area are shown in Fig. 5 and Table 5. The analysis of ACG6 is shown in Fig. 6 and Table 6.

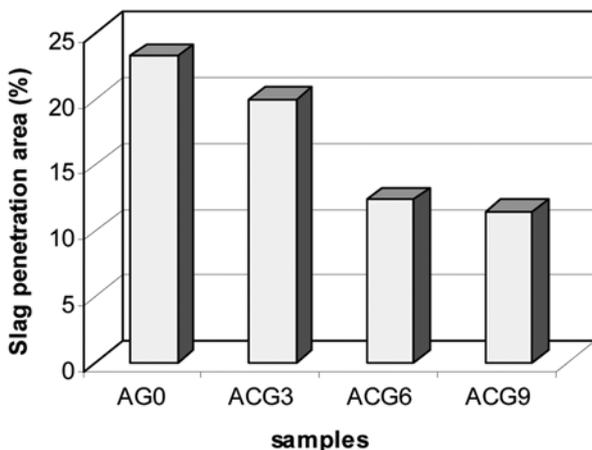


Fig. 4. Slag penetration areas in LCC's.

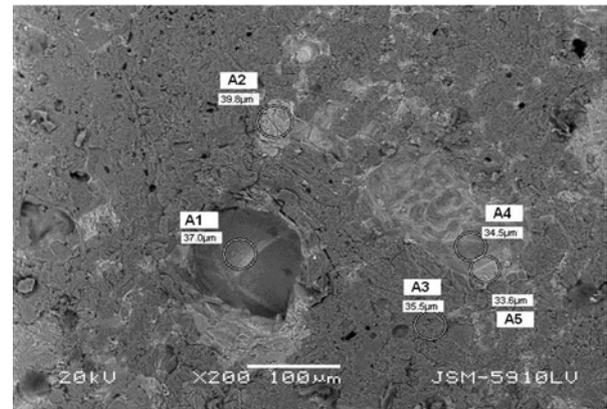


Fig. 5. SEM micrograph of the corroded area of AG0.

Table 5. EDS results of AG0

wt%	A1	A2	A3	A4	A5
O	37.44	45.26	46.18	51.68	50.22
Mg	0.53	0.30	-	-	0.32
Al	12.67	12.96	53.82	47.22	13.40
Si	8.30	16.75	-	-	16.35
Ca	7.4	20.97	-	-	16.62
Fn	3.50	1.27	-	-	1.29
Fe	30.42	2.48	-	1.10	1.80

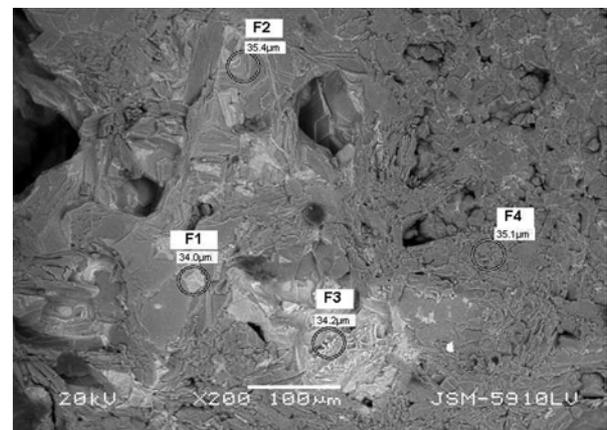


Fig. 6. SEM micrograph of the corroded area of AG6 which has 6 wt% alumina coated graphite.

Table 6. EDS results of AG6

wt%	F1	F2	F3	F4
C	4.12	4.54	3.58	5.70
O	33.63	45.51	35.87	48.45
Mg	1.81	0.81	1.40	-
Al	15.42	15.08	7.75	42.54
Si	4.48	5.90	5.49	-
Ca	9.24	15.21	17.40	3.31
Mn	2.67	1.93	3.69	-
Fe	28.62	11.01	24.82	-

Results and Discussion

As seen in the Table 1; the main refractory matrix (aggregate) comprises the castable mixture composition of 75 wt% tabular alumina, 13 wt% reactiv alumina, 5 wt% hydratable alumina, 5 wt% micro silica and 2 wt% calcium-aluminate cement. This selected composition is a formula suitable for standard use for commercial purposes. In order to improve the properties of the structure, particularly the slag resistance at steel melting temperatures by adding to the mixture alumina coated graphite powders of 3, 6, 9 wt%. Finally, water is added in order to render the mixture castable.

Based on the water that needs to be added to the non-graphite containing castable sample AG0 as seen in Table 2, this ratio in the ACG6 with 6 wt% supplementary coated graphite was higher by 46 wt%. Such a situation is caused as a result of the non-wettability of the hydrophobic graphite and its higher requirement of water. However, during the studies conducted by preparing uncoated graphite-supplemented mortar, the water required was higher by 65 wt% than for ACG0. This indicates that, as a result of coating with alumina, the water wettability could be improved. Its lower water content is also an advantage in terms of physical, mechanical and slag resistance since the uncoated graphite supplemented refractories will have less porosity after firing. AG0 has high bulk density and CCS because of its low apparent porosity and water absorption compared to the other samples (Table 3, Figs. 1 and 2).

The slag corrosion tests applied to the castable refractories according to DIN 51069-2 and at 1600 °C for 2 hours were explained above. In the course of the initial visual examinations carried (Figs 3 and 4) at a macroscopic level, it is seen that coated graphite supplemented refractory samples have a higher corrosion resistance to the slag as compared to non-supplemented AG0. The slag that penetrates into the refractory AG0 cannot achieve the same result in the other refractory samples, therefore, and overflows out of the crucible. Such a case is a result of the non-wettability of the graphite. The non-wettability of the graphite against the slag is an important feature for the refractory. At high temperatures, as a result of an increase in the wetting angle of the liquid slag contacting the surface of the graphite-containing refractory due to the surface tension, the effectiveness of the slag is

limited and diffusion of the slag into the refractory may be prevented.

In the Fig. 3, dissolution and infiltration areas in the interface of slag-refractory may be seen. The slag penetration depth of AG0 is higher compared to ACG3, ACG6 and ACG9 samples (Fig. 4).

When looking at the results of non-supplemented AG0 by SEM-EDS analysis, within the alumina matrix, components such as FeO, Fe₂O₃, MnO and SiO₂ as well as CaO from diffused slag can be observed. In the areas close to slag-refractory contact surface, called hot areas, it was seen that Fe- and Mn-concentrations were higher than Ca and Si concentrations and diffusion of Ca and Si extended to deeper areas than Fe and Mn. In the areas where Fe²⁺ and Fe³⁺ concentrations were high, the concentration of Mg²⁺ and Mn²⁺ which is scarce in the slag increases. Thus, as a result of the reaction of FeO, Fe₂O₃, MnO and MgO from the matrix with the reactions of Al₂O₃ in the matrix, complex spinel structure rich in ferrous (Fe, Mn, Mg).(Fe, Al)₂O₄ come into being. As seen in point A1 of Fig.5, the diameter of the complex spinel solid solution is over 100 µm. The melting temperature of the resulting complex spinel structure rich in iron is lower compared to the matrix. Thus it increases the effectiveness of the slag in this area. CaO and SiO₂ are seen around the spinel phase. These react with the Al³⁺ ions found in the spinel cage surfaces, and create the CA phases and CAS (calcium-alumina-silicate) phases.

The spinel reactions that are denser in the hot zone are replaced by the CAS phases towards the inner parts. The low melting temperature taking place in these areas and low glass-like silicate structure decrease the viscosity of the system, and further increase the slag penetration depth.

A similar chemical corrosion structure mechanism takes place in the coated graphite added refractories. However, due to non-wettability of the graphite in the refractories, it is observed that the effectiveness of the slag is kept to the limits in the slag-refractory interface. Also, while preventing the penetration of the glass-like solution, as a result of the reaction of CaO from the slag and Al₂O₃ of the matrix, it was found that CA (calcium-alumina) phases with relatively higher melting temperatures occurred (point F4 in the Fig. 6). The viscosity of the system increases and thus the penetration of the slag is prevented.

This formation is more evident in the coated graphite added samples. Actually, on observius point Fig. 6-F4, it may be seen that the phase that comes occurs is the CA₆ phase. CA₆, among the calcium-aluminate phases, is the one that shows the highest degree of refractoriness (T_M: 1803 °C) and is beneficial to the refractory. CA₆, as a phase with a high melting temperature, protects the refractory against the slag.

Conclusions

Alumina coated graphite (produced by a sol-gel method) additions have advantages against uncoated graphite.

These are; less water usage in a castable mixture and an increase in oxidation resistance at elevated temperatures [5]. By coating the graphite the slag-refractory resistance is greatly increased at working temperatures.

As a result, in physical, mechanical terms and in respect of the resistance against a steel slag, it was found that 6 wt% alumina coated graphite added castable refractories gave the best result and its usage is recommended in the wear linings contacting a steel slag.

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