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The effect of additives on the properties and microstructures of Al_2O_3-C refractories

M. N. KHEZRABADI
Materials Research Center, Jahad Daneshgahi, Ardakan-Yazd

J. JAVADPOUR*, H. R. REZAIE, R. NAGHIZADEH
Department of Materials Science and Engineering, Iran University of Science and Technolgy, Tehran, Iran
E-mail: javadpourj@iust.ac.ir

The effect of Al and Si additions on the properties and microstructure of Al_2O_3-C refractories has been studied. The results showed an increase in the strength and a decrease in porosity values with the increase in the Al content in the samples. The increase in firing temperature at a constant level of Al content had a deteriorating effect on the above mentioned properties. The oxidation resistance in the Al containing samples showed an improvement in the range of Al content studied in this work. Improvement in the oxidation resistance was also seen in the samples containing Si as additive. However, unlike the Al-case higher firing temperatures in the Si containing samples led to an increase in the strength and a decrease in the porosity values. The available thermodynamic data as well as x-ray diffraction (XRD) and scanning electron microscopy (SEM) were used in the interpretation of the experimental data.

1. Introduction

Alumina graphite refractories are widely used in the continious casting of steel [1]. The good thermal shock and corrosion resistance associated with the presence of carbon, make these type of refractories suitable candidate in the fabrication of sliding gate and stoppers used in the steel fabrication plants [2, 3].

The main drawback in alumina graphite refractories is their oxidation at high temperatures which leads to the deterioration of properties in refractories. One of the effective means of reducing the oxidation in this type of refractories has been the use of antioxidants [4–9].

Al and Si have been a popular choice with the industry because of their relative low cost and an acceptable performance. The formation of aluminum carbide and nitride phases in the Al-added samples resulted in oxidation resistance improvement in the refractory samples [10–11]. In the Si added samples the formation of SiC is thought to be the major cause of improvement in the properties [12–13]. In this paper thermodynamic considerations are applied to explain the physical, mechanical and oxidation resistance behaviour in the Al_2O_3 graphite samples with Al or Si as an additive.

2. Experimental procedure

The primary starting materials used in this work were Alcoa tabular alumina, chinese flake graphite and turkish novalak resin binder. The XRF (Philips PW 1480) chemical composition for the alumina and flake graphite is shown in Table I. Al and Si powders with more than 98% purity and particle size distribution less than 50 μm were used as antioxidants. Al_2O_3 and graphite content in the Al_2O_3-C samples were kept at 95 and 5 wt% respectively. The amount of novalak resin was 5 wt% of the total sum of the Al_2O_3 and graphite content in the samples.

The amount of antioxidant (Al or Si) was varied between 1 and 5 wt% of the total weight of the batch.

The raw materials were hand mixed and aged for 24 h prior to shaping. The aged powders was pressed uniaxially into cylindrical shape (40 mm height & 60 mm diameter) under the pressure of 150 MPa. Pressed samples were cured at 200°C for 14 h. Finally the samples were fired at 1450°C 3 h in a coke environment. The porosity and

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*Author to whom all correspondence should be addressed.

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TABLE I. Chemical compositions of the primary raw materials (wt%)

	Al_2O_3	C	Fe_2O_3	Na_2O	CaO	SiO_2
Tabular alumina	99.3	–	0.5	0.14	–	–
Flake graphite	0.55	96.5	0.75	–	0.15	1.50

cold crushing strength (CCS) of the samples were measured according to JIS(R 2205-02) and JIS(R-2206-01) standards respectively. In order to investigate the phase development, the Al and Si added samples were fired at 800, 1000, 1200 and 1400°C with 3 h of soaking at the indicated temperatures. The heated samples underwent porosity as well as structural and microstructral examination using a D4 Endeavor XRD and a cambridge S360 SEM unit. The oxidation resistance of the samples containing 0, 1, 3 and 5% of additives was studied by first firing the samples at 1450°C in a coke environment. This was followed by a heat treatment in an oxidizing atmosphere in the temperature range of 800–1400°C with the soaking time of 2 h at the maximum temperature. The difference in the weight of the samples before and after heating in oxidizing environment was taken as an indication for the oxidation resistance.

3. Results and discussion

Figs 1 and 2 show the effect of additive wt% on the apparent porosity and cold crushing strength respectively. Samples were fired at 1450°C in a coke environment. As shown in these figures the apparent porosity decreased and the strength increased with the addition of 1 to 5 wt% Al or Si into these samples.

The effect of temperature on the properties (porosity & CCS) for the samples containing 5 wt% Al or Si are presented in Figs 3 and 4. It is seen that in the case of Al-containing samples the porosity decreases and the strength increases as the firing temperature changes from 1150 to 1450°C. In the Si containing samples there is a sharp change in porosity and strength values at firing temperatures above 1300°C.

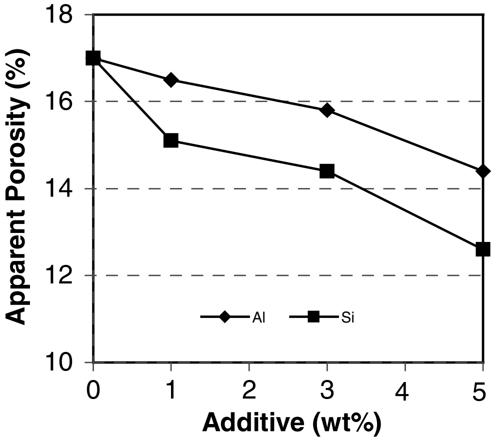

Figure 1 Variation of porosity with the percentage of additives for the samples fired at 1450°C.

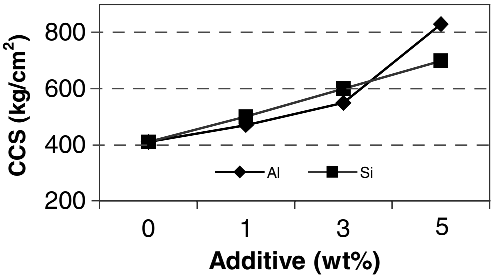

Figure 2 Variation of CCS with the percentage of additives for the samples fired at 1450°C.

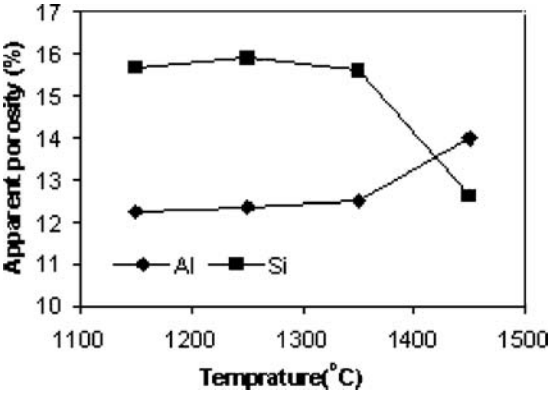

Figure 3 Variation of porosity as a function of firing temperature for the samples containing 5 wt% Al or Si.

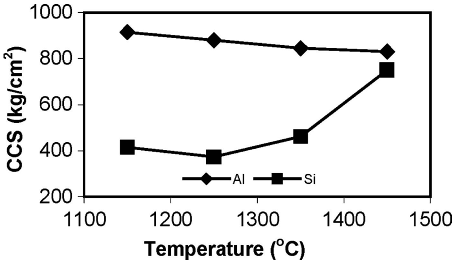

Figure 4 Variation of CCS as a function of firing temperature for the samples containing 5 wt% Al or Si.

The X-ray diffraction pattern for the sample containing 5 wt% Al fired at different temperatures is shown in Fig. 5. The pattern shows the presence of Al_4C_3 and AlN phases as a result of the reaction between Al and carbon. With the increase in the firing temperature the X-ray peak intensity associated with Al_4C_3 decreases while those related to Al_2O_3 show a slight increase.

The formation of SiC phase is observed in the samples containing 5 wt% Si at the firing temperature of 1250°C or higher (Fig. 6). Along with the formation of SiC phase, there is a decrease in the Si peak intensity as shown in

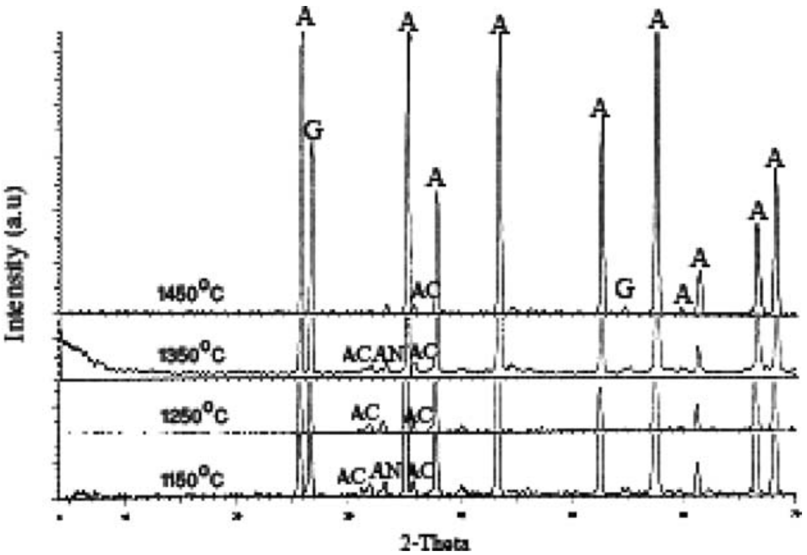

Figure 5 XRD patterns of samples containing 5 wt% Al fired at indicated temperatures in a coke bed. A, Al_2O_3; Ac, Al_4C_3; G, graphilte; AN, AlN.

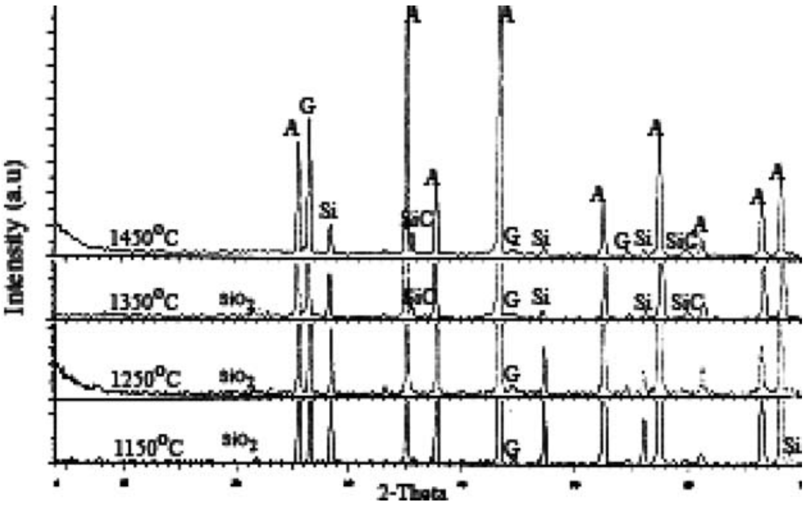

Figure 6 XRD patterns of samples containing 5 wt% Si fired at indicated temperatures in a coke bed. A, Al_2O_3; G, graphite.

this X-ray patterns. However, even at 1450°C there is still some unreacted Si in the micostructure. We also observed the formation of SiO_2 phase at lower firing temperatures. The intensity of the peak associated with this phase decreases with the increase in the firing temperature and disappeares completely after firing at 1450°C.

Fig. 7, is a SEM micrograph showing the fracture surface of a sample containing 5 wt% Al fired at 1450°C in a coke environment. The presence of plate like Al_4C_3 crystals is shown in the micrograph. The chemical composition of this phase was verified using EDS analysis.

SEM micrograph for the 5 wt% Si containing sample fired at 1450°C is presented in Fig. 8. The formation of SiC crystals as a result of reaction between Si and graphite is seen in this microstructure.

Fig. 9 shows the result of the oxidation resistance test for the Al containing samples. As indicated in this diagram the resistance to oxidation improves with the increase in the Al content in the sample. The improvement in the

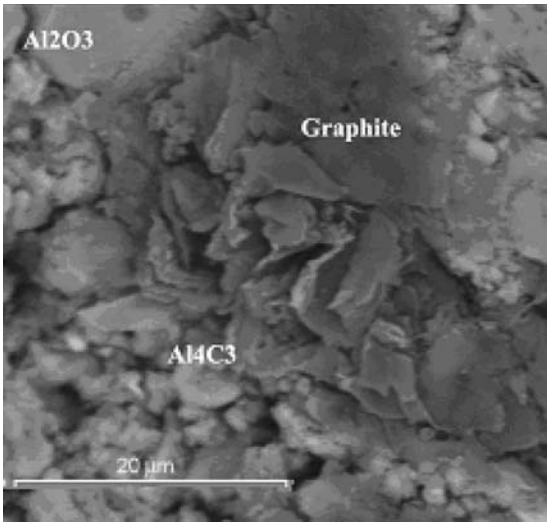

Figure 7 SEM micrograph showing the fracture surface of sample containing 5 wt% Al fired at 1450°C.

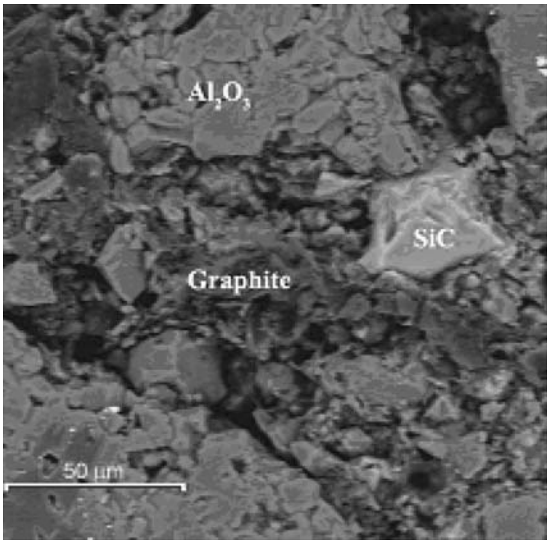

Figure 8 SEM micrograph of sample containing 5 wt% Si fired at 1450°C in a coke bed.

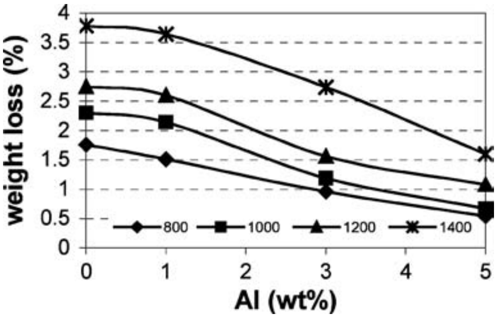

Figure 9 The results of the Oxidation resistance test for the Al containing samples.

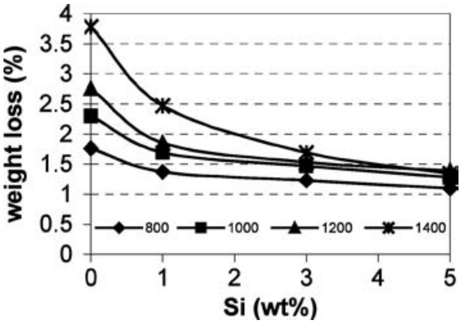

Figure 10 The results of the Oxidation resistance test for the Si containing samples.

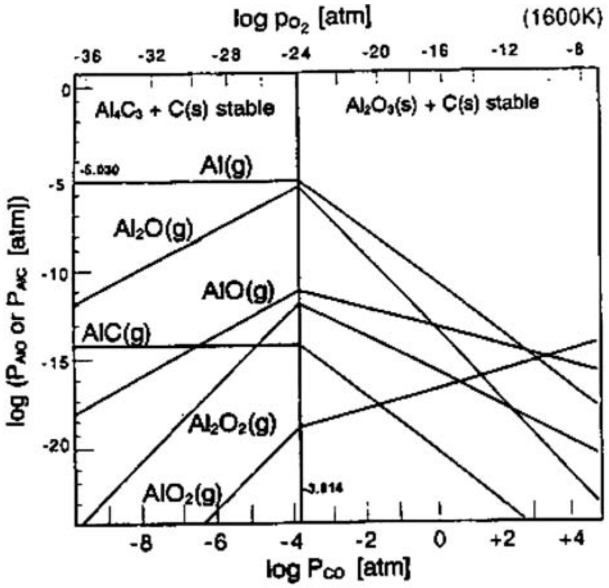

Figure 11 Thermodynamic data for Al–C–O system at 1600 K [11].

oxidation resistance becomes more significant at higher oxidation temperatures. The result of the oxidation test for the samples containing Si is shown in Fig. 10. As shown in this figure, at lower percentage of Si some improvement in the oxidation resistance is observed. However, the oxidation resistance did not improve significantly at higher Si levels.

Now the available thermodynamic data is used in explaining the effect of Al and Si addition on the properties of the refractory samples. The data used has been extracted from JANAF tables [11]. Fig. 11 shows the thermodynamic data for the Al–C–O system at 1600 K. As shown in this diagram Al(g) is the phase with highest partial pressure. Therefore the reaction between the Al-gas phase and graphite or N_2 may occur according to the following reactions:

$$4\text{Al(l, g)} + 3\text{C(s)} = \text{Al}_4\text{C}_3\text{(s)} \tag{1}$$

$$\text{Al(l, g)} + 1/2\text{N}_2\text{(g)} = \text{AlN(s)} \tag{2}$$

Formation of these phases in the microstructure are the reason for the improved strength in the samples. In fact the improvement in the properties is related to the plate and needle like morphologies of the carbide and nitride phase respectively [6, 11].

Since the firing of the samples is done in a coke atmosphere, the partial pressure of the CO gas in the samples can be assumed to be close to 1 atm. According to Fig. 11 the stable phase in this range of P_{CO} values is Al_2O_3. At this high partial pressure values of CO, Al_4C_3 is expected to react with CO according to the following reaction:

$$\text{Al}_4\text{C}_3\text{(s)} + 6\text{CO(g)} = \text{Al}_2\text{O}_3\text{(s)} + 3\text{C(s)} \tag{3}$$

Which is in agreement with the experimentally observed data, i.e. with the increase in the temprature there was a reduction in the amount of carbide phase and an increase in the amount of alumina phase (Fig. 5). Reduction in the amount of carbide phase leads to the degradation of properties in the samples. Another important point to note is that along with the formation of Al_2O_3 (reaction 3) there is precipitation of carbon phase in the microstructure which explains the improvement in the oxidation resistance in the Al containing samples.

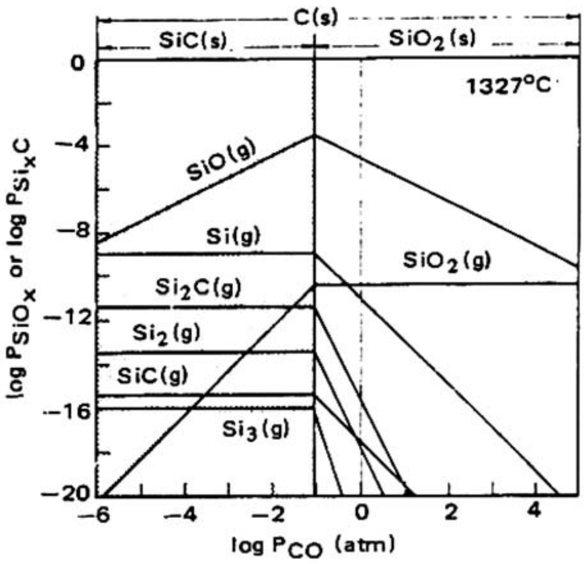

Figure 12 Thermodynamic data for Si–C–O system at 1600 K [6].

Fig. 12 shows the thermodynamic data for Si–C–O system at 1600 K. SiO(g) is the phase with the highest partial pressure in the system which may be the result of the following reactions within the sample:

$$2Si(s) + CO(g) = SiO(g) + SiC(s) \quad (4)$$

$$Si(s) + CO(g) = SiO(g) + C(s) \quad (5)$$

Based on the thermodynamic data shown in Fig. 12, at $P_{CO} = 1$ atm, SiO_2 is the most stable phase. However, the experimental results show the simultaneous presence of both SiC and SiO_2 in the samples. With the increase in the temperature, SiC becomes the more stable phase and SiO_2 disappears completely at 1450°C (Fig. 6). The simultaneous presence of SiC and SiO_2 within the sample is explained by the following reactions:

$$SiO(g) + CO(g) = SiO_2(s) + C(s) \quad (6)$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \quad (7)$$

The formation of SiC is a major factor in the improvement of properties. The special morphology of the SiC creates a ceramic bond between the particles which leads to increase in the strength. There is also a volume expansion associated with the formation of SiC that reduces the total porosity in the samples. Our results show that the formation of SiC begins around 1300°C. However, there is some unreacted Si even at 1450°C. Complete elimination of Si using an optimum firing temperature is expected to improve the properties even further.

To explain the oxidation resistance behavior in the Si containing samples, it should be mentioned that depending on the partial pressure of oxygen and the temperature of oxidation, the oxidation process may be classified as passive or active (Fig. 13). In the passive oxidation a layer of SiO_2 film forms on the SiC particles with the retarding effect on the oxidation. In an active oxidation, the oxidation continues by the removal of SiO(g) from the sample. In an oxidation test there is an increase in the partial pressure of CO within the sample which is due to carbon oxidation. Thus, the oxidation of SiC within the sample can take the active form through the following reaction:

$$SiC(s) + CO(g) = SiO(g) + 2C(s) \quad (8)$$

On the other hand because of the high PO_2 in the furnace atmosphere, the PO_2 in the regions near the surface of the sample will also be high and thus a passive type of

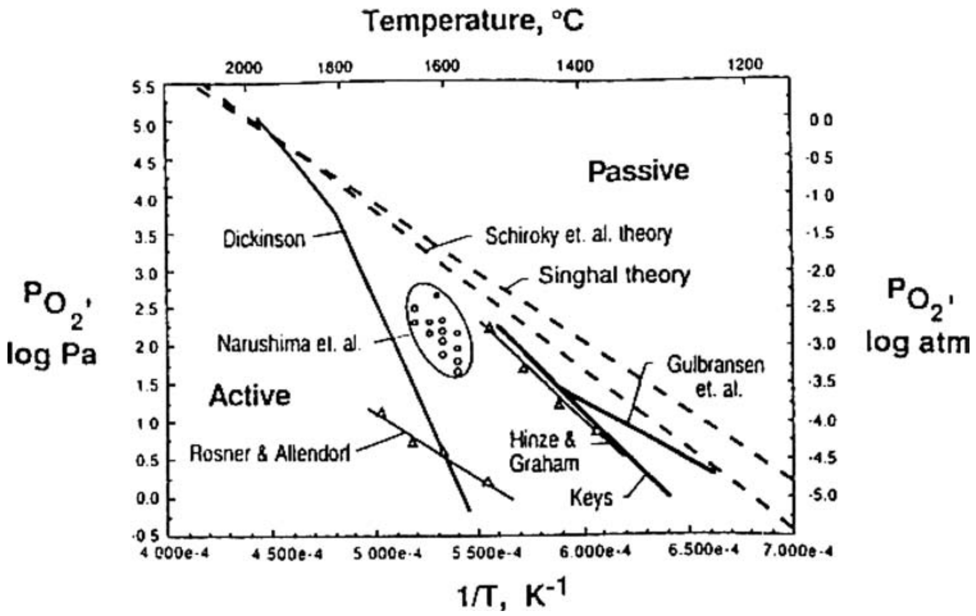

Figure 13 Active and passive oxidation of SiC [14].

oxidation is expected near the surface, i.e. the following reaction takes place near the sample surface:

$$SiO(g) + 1/2O_2 = SiO_2(s) \quad (9)$$

The formation of SiO_2 layer near the surface will have a retarding effect on the oxidation. As the Si content in the sample increases the layer becomes thicker and since the oxidation rate is controlled by the diffusion of oxygen through this layer, eventually a constant rate of oxidation is reached at higher Si contents.

4. Conclusions

The effect of Al and Si addition on the properties and microstructure of alumina graphite refractories has been investigted. The main results drawn from this study are as follows:

1. The presence of Al has a positive effect on the physical and mechanical properties of the Al_2O_3-graphite refractory samples. However, it should be kept in mind that the properties are sensitive to firing temperature, i.e. the properties degrade at higher firing temperatures.
2. The formation of Al-carbide and nitride phases are beleived to be the cause of property improvement in the Al containing samples. In the Si-added samples the formation of SiC is the main factor causing improvement in the properties.
3. Decrease in the amount of Al_4C_3 phase with the increase in the firing temperature lowers the strength in the Al_2O_3-graphite sample.
4. The use of Al or Si reduces the oxidation rate in the Al_2O_3-graphite refractory sample. However, the formation of SiO_2 layer at the surface limits the improvement in the oxidation resistance at higher percentage of Si addition.

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