

The Influence of Al and Si Additives on the Microstructure and Mechanical Properties of Low-Carbon MgO-C Refractories

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Abstract

The mechanical properties of low-carbon MgO-C refractories strongly depend on the formation of ceramic phases (e.g. their amounts, distribution and morphologies) in the matrix. In the present work, the influence of Al and Si additives on the phase composition, microstructure and mechanical properties of low-carbon MgO-C refractories (1 wt% flaky graphite) was investigated by means of X-ray diffraction, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, three-point bending and thermal shock tests. The results showed that Al_4C_3 whiskers and MgAl_2O_4 particles formed *in-situ* in the specimens after firing at 1000 °C and 1200 °C when Al and Si additives were incorporated simultaneously into the specimens. Up to 1400 °C, many SiC whiskers and plate-like AlN as well as MgAl_2O_4 in the form of hollow MgO-rich whiskers and particles appeared. However, few SiC whiskers and many Mg_2SiO_4 particles existed in the specimen fired at 1200 °C and lots of Mg_2SiO_4 particles formed at 1400 °C when Si powder was used as the additive. These ceramic phases unquestionably influenced the mechanical properties of low-carbon MgO-C refractories. Improved mechanical properties and thermal shock resistance were achieved for the specimen with Al and Si additives compared with those of the specimen containing Si powder.

Keywords: *In-situ*-formed ceramic phases, mechanical properties, thermal shock resistance, MgO-C refractories

1. Introduction

MgO-C refractories are widely used in steelmaking vessels, e.g. converters, electric arc furnaces, ladles and RH vacuum degassers owing to their outstanding corrosion resistance and thermal shock resistance^{1–4}. Usually, they contain a high amount of 12–20 wt% C (typically in the form of flaky graphite as the main carbon source), which leads to certain disadvantages such as inferior oxidation resistance, high carbon pick-up in molten steel, higher heat loss and higher CO_x emissions^{5,6}. To solve these problems, it is of great importance to develop low-carbon MgO-C refractories (lower than 8 wt% carbon content) and ultra-low-carbon refractories (lower than 3 wt% carbon content). However, the mechanical properties of the refractories deteriorate when the graphite content in the matrix is reduced. This especially affects the thermal shock resistance of the refractories. The microstructure of low-carbon refractories must therefore be optimized. In the past decade, nano-sized carbon sources have often been added to low-carbon refractories to improve their microstructure and to further enhance their mechanical properties⁷. In fact, the *in-situ*-formed ceramic phases (amounts, distribution and morphologies) in the matrix also play a vital role in the improvement of the mechanical properties of low-carbon refractories.

Generally, the *in-situ*-formed ceramic phases depend strongly on the incorporation of various additives as well as carbon sources and catalysts in carbon-containing refractories^{8–10}. For example, Si additive was responsible for *in-situ*-formed SiC whiskers, and microsilica additive mainly dominated the growth of needle-like mullite in Al_2O_3 -C refractories¹¹. In addition, *in-situ*-formed SiC whiskers can be easily produced using flaky graphite as the carbon source and SiC spherical particles grew in the case of carbon black¹². Also, graphite oxide nanosheets (0.5 wt%) or expanded graphite (0.2 wt%) had a positive influence on the formation of more AlN bonding phase to improve the mechanical strengths and thermal shock resistance compared with the refractories containing only flaky graphite at elevated temperatures^{13,14}. Furthermore, the addition of catalysts or catalytic precursors promoted the growth of ceramic whiskers at high temperatures. The growth of MgAl_2O_4 whiskers can be observed in MgO-C refractories with the addition of ferrocene or nano-sized metallic Ni^{15–17}. And Ni-containing precursor accelerated the growth of MgO whiskers, which further enhanced the mechanical properties of low-carbon MgO-C refractories¹⁸.

In fact, Si powders are commonly added to MgO-C refractories to protect the carbon in the refractories prior to carbon oxidation and to further improve their mechanical properties^{2,19}. However, Si powder is transformed com-

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pletely into Mg_2SiO_4 particles at elevated temperatures, which leads to MgO-C refractories exhibiting low mechanical strength and poor thermal shock resistance. Also, our previous work showed that the use of Al and Si additives promoted the growth of SiC whiskers in carbon refractories for blast furnaces and thus enhanced their mechanical properties²⁰. So, in the present work, metallic Al and Si powders are incorporated simultaneously into low-carbon MgO-C refractories to improve their mechanical properties; also, their microstructure and mechanical properties are assessed as part of a comparative investigation with those of low-carbon MgO-C refractories containing Si powder.

II. Experimental

(1) Preparation of MgO-C refractory specimens

Fused magnesia (3–1 mm, 1–0 mm and <0.088 mm, 98 wt% MgO, Dashiqiao, China), metallic aluminum (<0.088 mm, 98 wt% Al, Xinxiang, China), silicon powder (<0.045 mm, 98 wt% Si, Anyang, China), and flaky graphite (FG, <0.0774 mm, 97.5 wt% fixed carbon, Qingdao, China) were used as raw materials. Thermosetting phenolic resins, one in liquid form (36 wt% carbon yield, Zibo, China) and one in powder form (55 wt% carbon yield, Zibo, China) were used as binder. The investigated MgO-C compositions with varying additives are presented in Table 1. All the compositions were mixed for 30 min in a mixer with a rotating speed of 80–100 rpm. After kneading, bar-shaped specimens (25 mm × 25 mm × 140 mm) were compacted under a pressure of 150 MPa and then cured at 200 °C for 24 h. Finally, the as-prepared specimens were treated at a heating rate of 5 K/min to 1000 °C, 1200 °C and 1400 °C for 3 h in a saggar filled with coke grit, respectively.

Table 1: Investigated MgO-C compositions

Raw materials	Compositions (wt%)	
	S2	A2S2
Fused magnesia aggregate	70	70
Magnesia powder	27	25
Flaky graphite	1	1
Si powder	2	2
Metallic Al	-	2
Phenolic resin powder	+1	+1
Liquid phenolic resin	+4	+4

(2) Tests and characterization methods

The phase composition and microstructure of the MgO-C specimens were analyzed and observed by means of x-ray diffraction (XRD, X' Pert Pro, Philips, Eindhoven, the Netherlands; using Ni-filtered, Cu K_α radiation at a scanning speed of 2 deg/min and a temperature of 16 °C) and field emission scanning electron microscopy (FES-EM, Nova 400 NanoSEM, FEI Company, USA) coupled with energy-dispersive x-ray spectroscopy (EDS, INCA

IE 350 PentaFET X-3, Oxford, UK), respectively. The cold modulus of rupture (CMOR) and flexural modulus (FM) of the MgO-C specimens after firing at various temperatures were measured in a three-point bending test at ambient temperature with a span of 100 mm and a loading rate of 0.5 mm/min by means of an electronic digital control system (EDC 120, DOLI Company, Germany). The force-displacement curve of each refractory specimen was recorded simultaneously during the test. The bulk density (BD) and apparent porosity (AP) of MgO-C specimens were measured according to the Archimedes' principle with kerosene as the medium. Also, high modulus of rupture (HMOR) of MgO-C specimens after treatment at 200 °C was measured in a reducing atmosphere in a three-point bending test; the testing temperature was 1400 °C and the soaking time was 30 min.

The thermal shock resistance of the specimens after firing at 1400 °C was tested according to the following method. The specimens were heated in a coke bed up to 1100 °C at a heating rate of 5 K/min, and soaked at this temperature for 30 min. The specimens were then taken out and quickly quenched in an oil bath; the purpose of using an oil bath instead of a water bath was to prevent oxidation and hydration of the specimens. After one thermal shock cycle, the deterioration of the mechanical properties of the specimens was assessed in a three-point bending test. The residual strength ratio of CMOR was calculated based on the change in CMOR before and after thermal shock, i.e. the residual strength ratio of $\text{CMOR} = 100 \cdot \text{CMOR}_{\text{TS}} / \text{CMOR}$, where CMOR and CMOR_{TS} were the CMOR before and after one thermal shock cycle, respectively.

(3) Thermodynamic calculation

To predict the phase evolution of MgO-C refractories containing different additives at various temperatures, equilibrium thermodynamic calculations were conducted using the Equilib Module of the FactSage® software (version 6.2)²¹. The calculations were made for an atmosphere of 0.35 atm CO and 0.65 atm N_2 ^{2, 22}, and the parameter alpha was set as the weight ratio of atmosphere gas to specimen. The calculations considered 100 g of refractory and changed successively the additions of the atmosphere (increase in alpha). For instance, when alpha = 1.00, the calculation was performed with 100 g refractory and 10 g atmosphere. The predicted results were plotted as log grams of species as a function of alpha.

III. Results

(1) Phase composition

In order to clearly understand the effect of different additives and temperature on the phase compositions, XRD patterns of MgO-C specimens (S2 and A2S2) fired at different temperatures were measured and are shown in Fig. 1. In specimen S2 containing Si powder (Fig. 1a), periclase, graphite and Si phases were detected after firing at 1000 °C, indicating no new ceramic phase formed at this temperature. At 1200 °C, the peak intensity of Si phase decreased dramatically while SiC and forsterite phases formed. With a further increase in the temperature

to 1400 °C, Si phase disappeared completely and the peak intensity of the forsterite phase increased. As for specimen A2S2 where Al and Si were added simultaneously (Fig. 1b), Al phase disappeared whereas spinel phase appeared after firing at 1000 °C, apart from periclase, graphite and Si phases as starting materials. At 1200 °C, the peak intensity of Si phase decreased while SiC phase began to form, and the amounts of spinel phase increased. Above 1200 °C, Si phase disappeared while AlN phase formed, and the peak intensity of SiC phase increased.

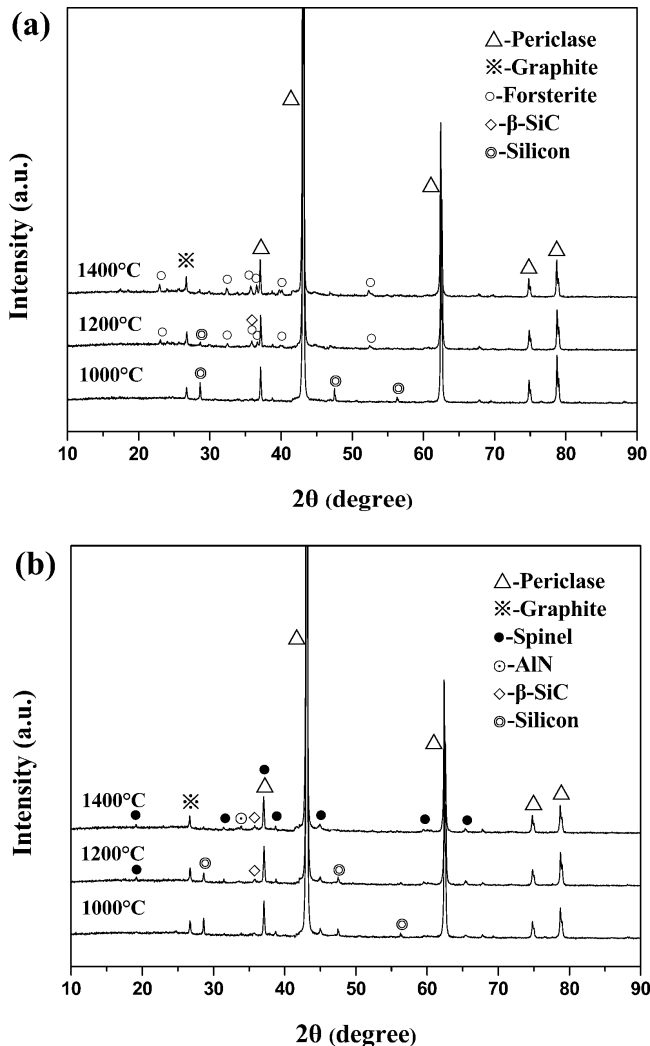


Fig. 1: XRD patterns of MgO-C specimens fired at various temperatures: (a) specimen S2 and (b) specimen A2S2.

(2) Microstructure

The SEM micrographs of MgO-C specimens containing different additives are presented in Figs. 2 and 3, respectively. As for specimen S2, no new ceramic phases formed in the matrix after firing at 1000 °C (Fig. 2a). At 1200 °C (Fig. 2b), a small number of SiC whiskers with a diameter of 50–100 nm and a length of up to several micrometers were observed. Also, some Mg_2SiO_4 particles began to appear in the matrix, which was confirmed with XRD and EDS analysis. As the firing temperature increased to 1400 °C, a great number of irregular Mg_2SiO_4 particles interlocked with each other and were distributed in the matrix and on the surface of magnesia particles (Fig. 2c).

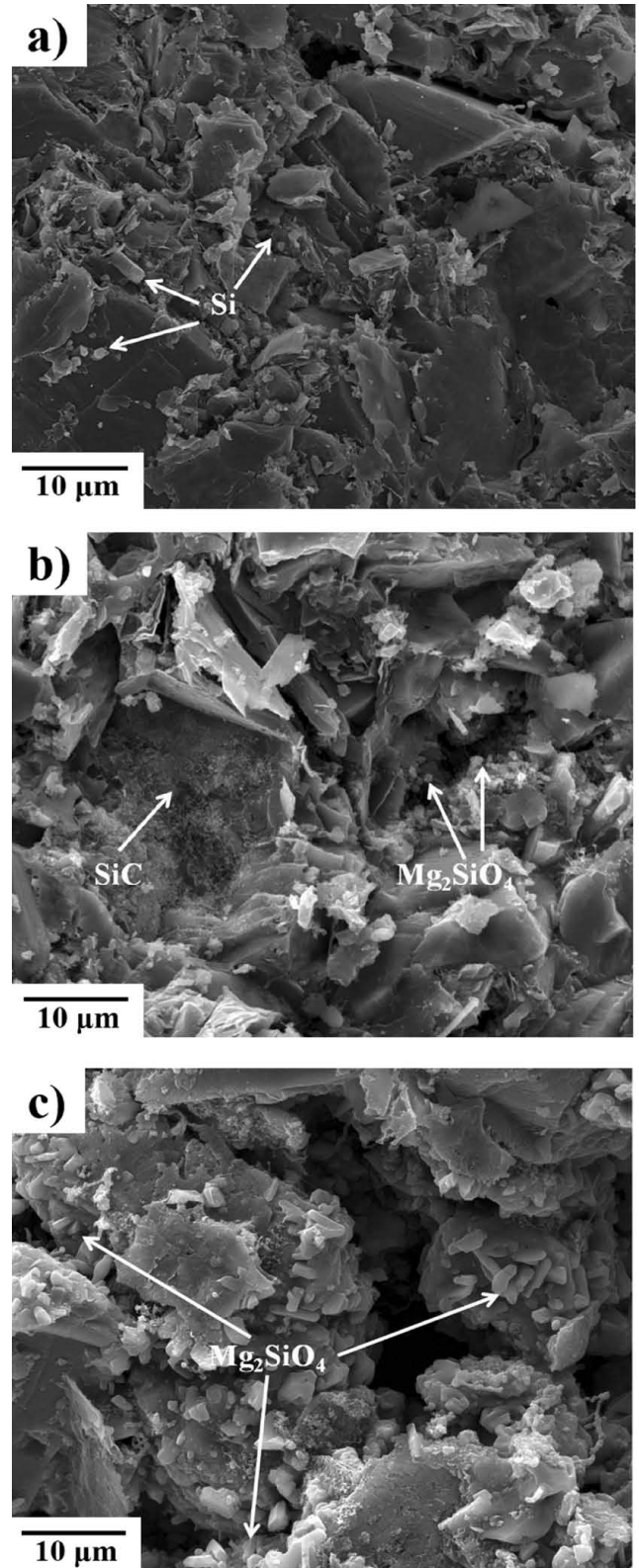


Fig. 2: SEM micrographs of the specimen S2 fired at various temperatures: (a) 1000 °C, (b) 1200 °C and (c) 1400 °C.

With regard to specimen A2S2, Al_2C_3 whiskers and MgAl_2O_4 particles were observed in the matrix where Al particles were originally located when the firing temperature was 1000 °C (Fig. 3a), as identified by means of EDS analysis. Similarly, they were found at 1200 °C (Fig. 3b). The results were in agreement with those reported by other researchers^{2,7,10,13,14}. When the firing temperature was 1400 °C, besides MgAl_2O_4 particles, many

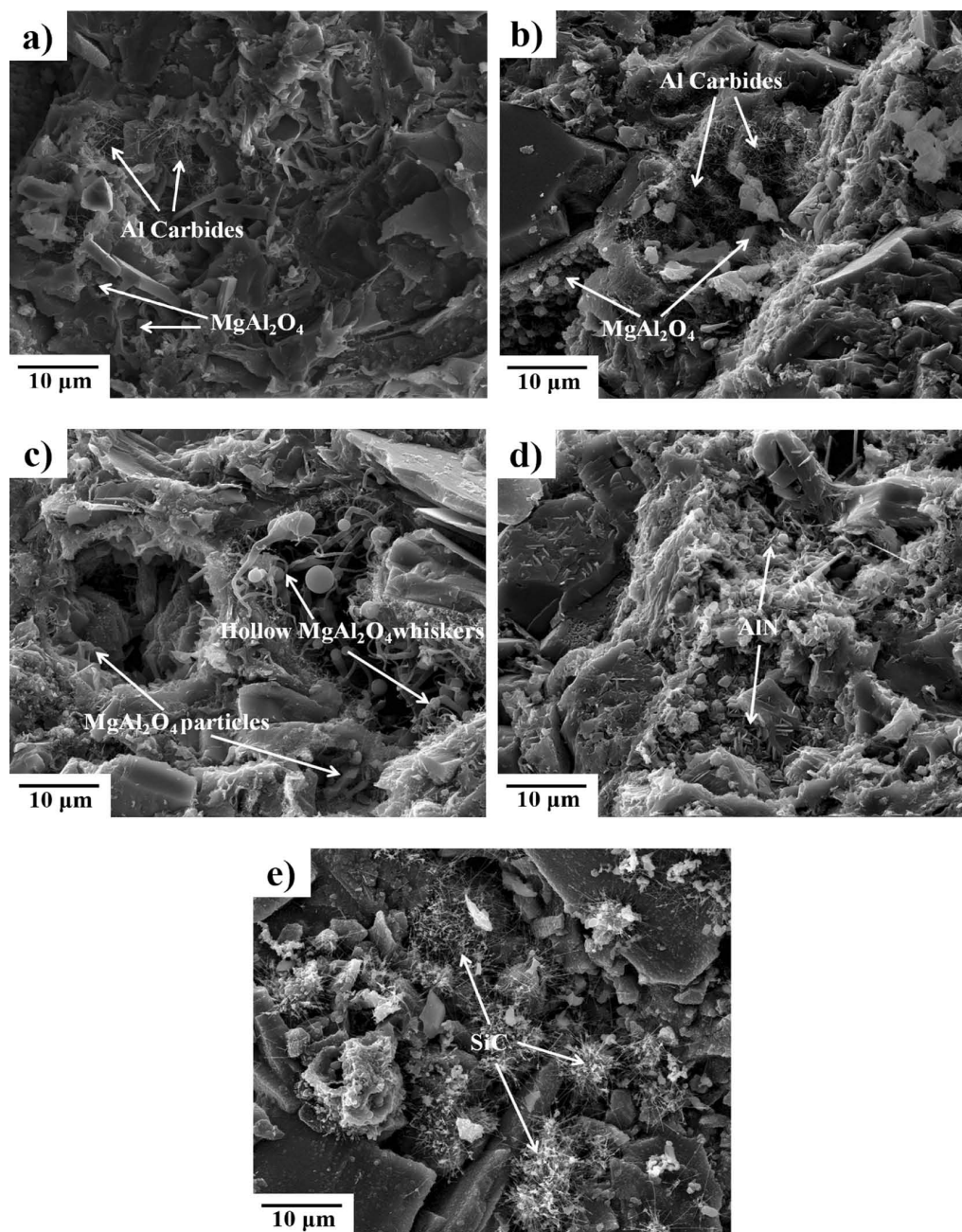


Fig. 3: SEM micrographs of the specimen A2S2 fired at various temperatures: (a) 1000 °C, (b) 1200 °C and (c) – (e) 1400 °C.

tadpole-like products appeared in the matrix and on the surface of magnesia particles (Fig. 3c); they were confirmed as MgO-rich spinel with XRD and EDS analysis and judged to have a hollow structure, which was also reported in our previous study²³. Also, large numbers of plate-like AlN (confirmed by means of EDS and XRD analysis, similar to other investigations^{13, 14, 24, 25}) appeared in the matrix (Fig. 3d); additionally, some SiC whiskers with a diameter of 50–100 nm and a length of up to 10 μm were found (Fig. 3e), which was different from the case of specimens S2 after firing at this temperature.

(3) Mechanical properties

The difference in the microstructure (*in-situ*-formed ceramic phases and their morphologies) may lead to a change in the mechanical properties of MgO-C refracto-

ries. Therefore, the cold mechanical properties of MgO-C specimens were measured in a three-point bending test at room temperature. The CMOR and FM of MgO-C specimens are shown in Table 2. The CMOR and FM of the specimens treated at 200 °C showed the highest values among the specimens treated at various temperatures. However, the CMOR and FM of all the specimens fired at 1000 °C decreased simultaneously owing to the pyrolysis of the resins. Cold mechanical properties of MgO-C specimens fired at 1200 °C were close to those of the specimens fired at 1000 °C. Nevertheless, at 1400 °C, the CMOR of all the specimens increased and the change of specimen S2 was more obvious. Furthermore, the specimens A2S2 had much higher CMOR values at all the firing temperatures, which were related to the physical properties of MgO-C specimens containing different additives (Table 3).

Table 2: Cold modulus of rupture (CMOR) and flexural modulus (FM) of MgO-C compositions treated at various temperatures.

Temperature	Properties	S2	A2S2
200 °C	CMOR (MPa)	37.65±0.88	40.27±1.15
	FM (GPa)	7.94±0.32	7.21±0.06
1000 °C	CMOR (MPa)	4.09±0.25	7.54±0.59
	FM (GPa)	1.61±0.14	1.99±0.24
1200 °C	CMOR (MPa)	4.35±0.07	8.66±0.17
	FM (GPa)	1.14±0.08	2.23±0.04
1400 °C	CMOR (MPa)	7.28±0.17	9.65±0.47
	FM (GPa)	1.60±0.01	2.36±0.12

Fig. 4 shows the force-displacement curves of MgO-C specimens containing different additives. Apparently, the changes of forces and displacements have a similar tendency to that of the CMOR and FM. Also, specimen A2S2

presented much larger displacement compared with specimen S2 at all heat treatment temperatures.

Table 3: Bulk density (BD) and apparent porosity (AP) of MgO-C compositions treated at various temperatures.

Temperature	Properties	S2	A2S2
200 °C	BD (g/cm ³)	2.93±0.01	2.92±0.00
	AP (%)	9.6±0.2	10.1±0.1
1000 °C	BD (g/cm ³)	2.84±0.00	2.87±0.01
	AP (%)	16.3±0.1	13.6±0.1
1200 °C	BD (g/cm ³)	2.84±0.01	2.86±0.00
	AP (%)	16.4±0.4	14.0±0.1
1400 °C	BD (g/cm ³)	2.83±0.01	2.85±0.01
	AP (%)	16.6±0.3	16.0±0.2

In addition, the hot modulus of rupture (HMOR) of MgO-C specimens at 1400 °C is shown in Fig. 5. Specimen A2S2 exhibited a higher HMOR value of 20.32 MPa in comparison with that of specimen S2.

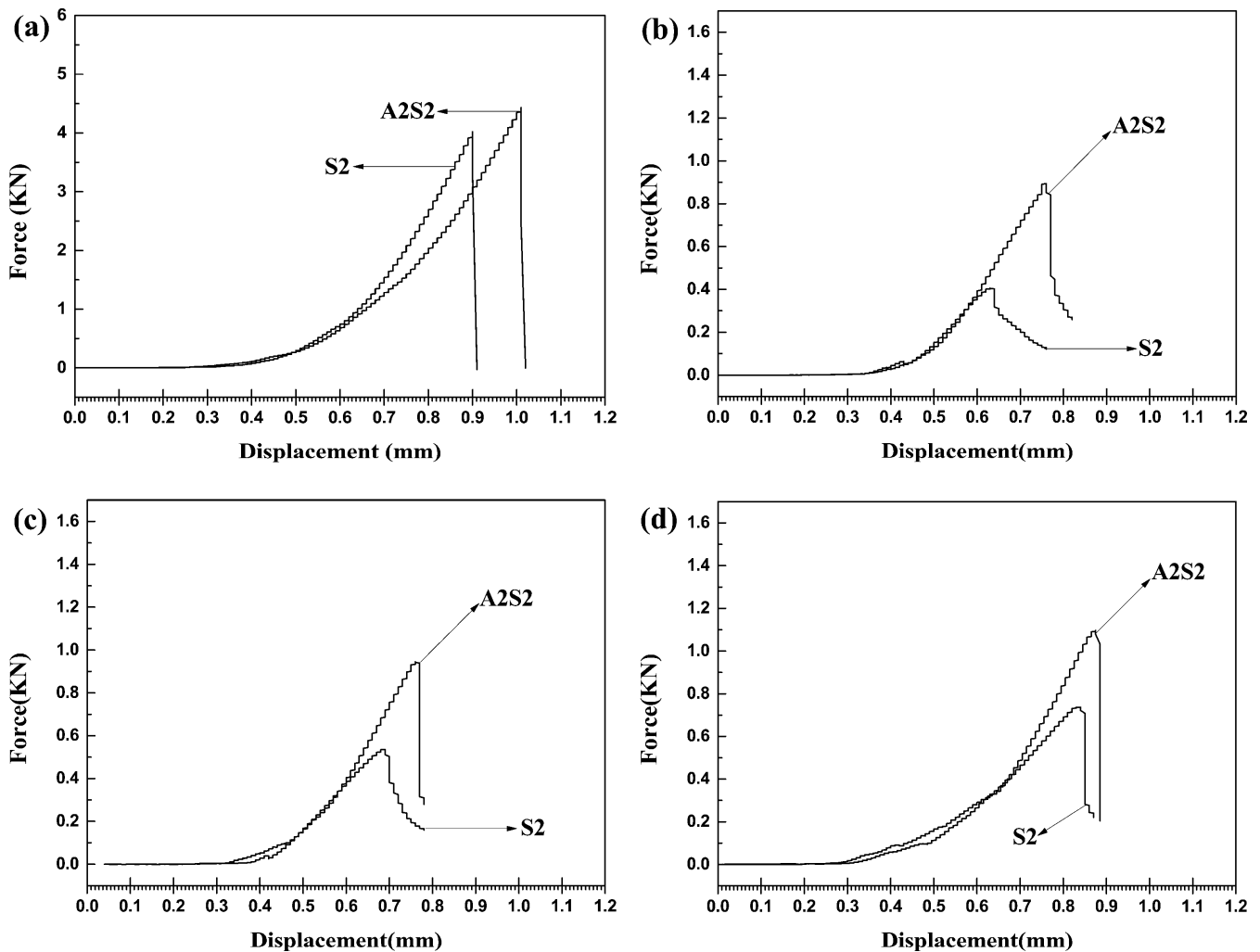


Fig. 4: Force-displacement curves of MgO-C specimens fired at various temperatures: (a) 200 °C, (b) 1000 °C, (c) 1200 °C and (d) 1400 °C.

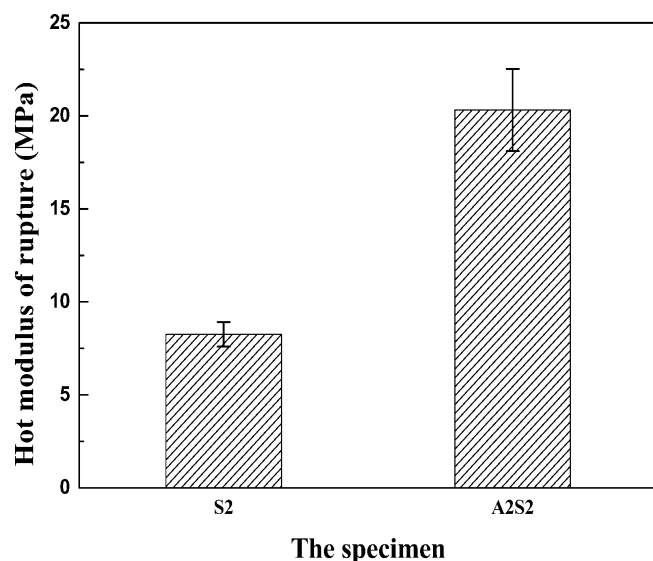


Fig. 5: Hot modulus of rupture of MgO-C specimens.

(4) Thermal shock resistance

Concerning the thermal shock behavior of MgO-C specimens after firing at 1400 °C, expressed by the residual CMOR after one thermal shock cycle (named CMOR_{TS}), the results are shown in Fig. 6. The higher CMOR_{TS} and residual strength ratio were 6.72 MPa and 69.74 %, respectively, for specimen A2S2, indicating that MgO-C specimens containing both Al and Si additives can withstand greater thermal shock compared to the specimen containing Si powder.

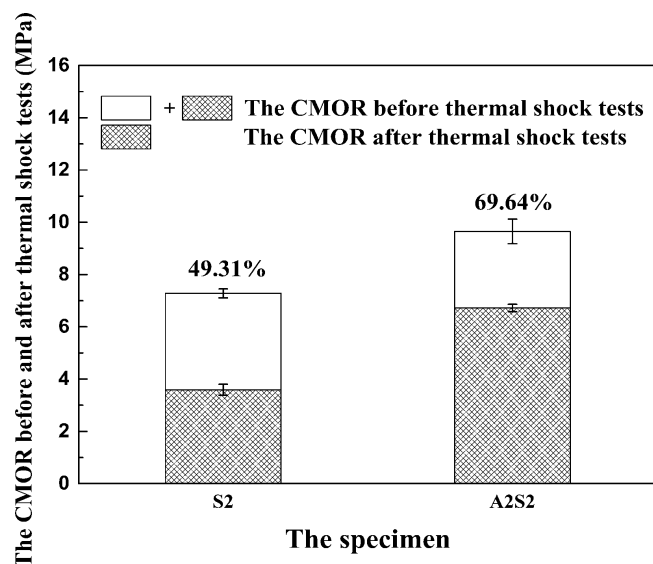


Fig. 6: Cold modulus of rupture (CMOR) of MgO-C specimens before and after thermal shocks and their residual strength ratio.

IV. Discussion

Thermodynamic analysis was undertaken to predict those phases formed in MgO-C specimens containing different additives at 1400 °C, and the result is shown in Fig. 7. The phase evolution in the systems is closely related to the alpha value. In a word, SiC, Mg₂SiO₄ and Si₃N₄ can form in the Si-added MgO-C specimen, while Al₄C₃, AlN

and MgAl₂O₄ can be also found for MgO-C specimens with Al and Si additives besides SiC, Mg₂SiO₄ and Si₃N₄. It is worth noting that the amount of Mg₂SiO₄ began to increase when the alpha values were 0 and 0.16, respectively, for the specimen with added Si and the specimen containing Al and Si additives, indicating that the addition of Al prohibited the formation of Mg₂SiO₄ and thus kept SiC stable. All the new phases in MgO-C refractories at elevated temperatures calculated with the FactSage® software are almost consistent with the experimental results, although Si₃N₄ phase was not detected for the Si-added specimen, and Si₃N₄ as well as Mg₂SiO₄ phases were not found for the specimen containing Al and Si additives. The occurrence might be attributed either to the low amounts formed or to the restriction of the kinetic factors^{2,22}.

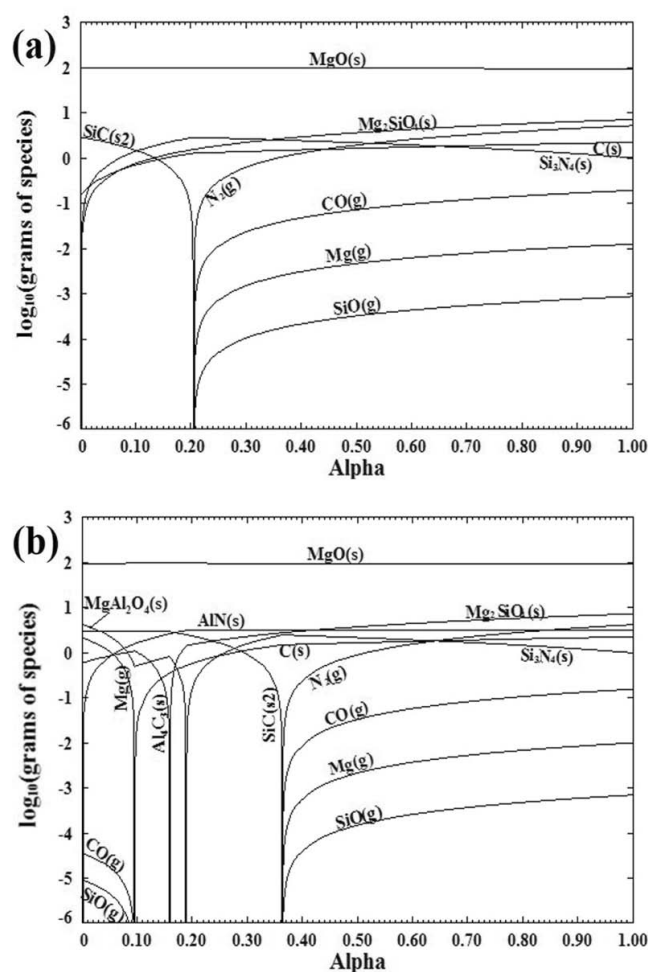
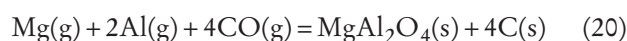
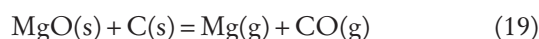
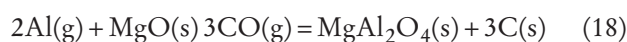
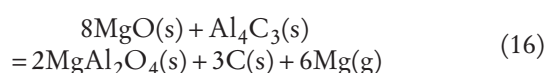
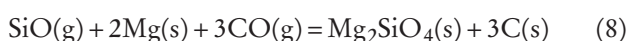
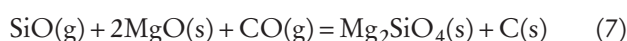
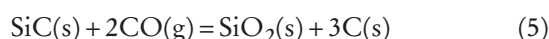
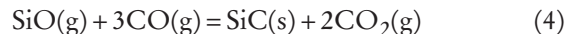
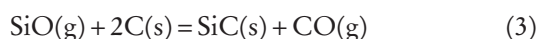
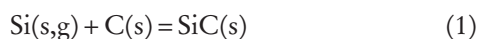


Fig. 7: Phase changes of the specimens S2 (a) and A2S2 (b) at 1400 °C.

On the basis of XRD analysis and microstructure observations, it can be concluded that the *in-situ* formation of ceramic phases is influenced by the additives used and firing temperature. For the Si-added specimen, no new ceramic phase formed at 1000 °C. However, SiC whiskers and Mg₂SiO₄ particles began to form at 1200 °C by the reactions (1) – (4) and (5) – (6), respectively. At 1400 °C, SiC phase disappeared owing to their transformation into SiO₂ via reaction (5), which thus led to the formation of more Mg₂SiO₄ particles; also, reactions (7) – (8) contributed to their greater formation

in the matrix at 1400 °C. With regard to the specimen containing Al and Si additives, at 1000 °C and 1200 °C, Al_4C_3 whiskers and MgAl_2O_4 particles formed via reactions (9) – (11) and (12) – (18), respectively. At 1400 °C, besides MgAl_2O_4 particles [reactions (12) – (18)], many hollow MgO-rich MgAl_2O_4 whiskers formed in the matrix and on the surfaces of magnesia particles, whose growth mechanism was discussed in detail in our previous study²³. Briefly, the hollow whiskers were dominated by the capillary transportation from liquid Al at elevated temperatures. In addition, lots of plate-like AlN formed in the matrix via reactions (21) – (22). Also, reactions (1) – (4) led to the growth of SiC whiskers. It is worth mentioning that Mg_2SiO_4 particles were not detected for the specimen with Al and Si as additives at any of the heat treatment temperatures while they began to form after firing at 1200 °C and grew dramatically at 1400 °C in the case of the specimen with added Si. The reason is that the addition of Al reduces the partial pressure of CO in the inner part of the specimen with added Al and Si additives²⁰, and thus the reaction between SiC and CO is inhibited, which leads to the presence of SiC whiskers as well as the absence of Mg_2SiO_4 particles in the specimen after firing at 1400 °C.



Undoubtedly, the formation of ceramic phases (amounts, distribution and morphologies) would result in a significant influence on the mechanical properties and thermal shock resistance of MgO-C refractories. At 1000 °C, the CMOR of specimen A2S2 was higher than that of specimen S2 owing to the fact that Al_4C_3 whiskers and MgAl_2O_4 particles formed in specimen A2S2 while no new ceramic phase formed in specimen S2. At 1200 °C, the CMOR of specimen S2 improved slightly owing to the formation of few SiC whiskers and Mg_2SiO_4 particles, but was still lower than that of specimen A2S2. With an increase in the temperature to 1400 °C, the combined effect of plate-like AlN, SiC whiskers, MgAl_2O_4 particles and MgO-rich MgAl_2O_4 whiskers contributed to the much higher CMOR of specimen A2S2. Similarly, the higher HMOR and improved thermal shock resistance resulted for specimen A2S2 because of the stronger ceramic bonding from plate-like AlN, SiC whiskers, hollow MgO-rich MgAl_2O_4 whiskers and MgAl_2O_4 particles in the matrix. The formation of hollow MgO-rich MgAl_2O_4 whiskers may give rise to improved mechanical strength and thermal shock resistance of specimen A2S2, which was in agreement with the findings of other researchers^{26,27}. Also, only Mg_2SiO_4 particles bonded in specimen S2 exhibited much lower HMOR and worse thermal shock resistance, suggesting that the combination of particle-bonded and one-dimensional product-bonded matrix would be helpful for the improvement of the mechanical properties and thermal shock resistance of the refractories.

V. Conclusions

The influence of Al and Si additives on the microstructure, mechanical properties and thermal shock resistance of low carbon MgO-C refractories was investigated in this work. The main conclusions are as follows:

(1) The additives used and firing temperature played a very important role in the *in-situ* formation of ceramic phases in low-carbon MgO-C refractories. For the specimens with added Al and Si additives, Al_4C_3 whiskers and MgAl_2O_4 particles grew after firing at 1000 °C and 1200 °C, and many SiC whiskers and plate-like AlN formed at 1400 °C as well as MgAl_2O_4 particles and hollow MgO-rich MgAl_2O_4 whiskers. In the specimens with added Si powder, the Si powder did not react at 1000 °C, but transformed into a few SiC whiskers and Mg_2SiO_4 particles at 1200 °C and lots of Mg_2SiO_4 particles at 1400 °C, respectively.

(2) The mechanical properties and thermal shock resistance of low-carbon MgO-C refractories were mainly influenced by the amounts, distribution and morphologies of ceramic phases formed in the materials. The synergistic effect of plate-like AlN, SiC whiskers, hollow MgO-rich MgAl_2O_4 whiskers and MgAl_2O_4 particles in the matrix led to better mechanical properties and thermal shock resistance of low-carbon MgO-C refractories with Al and Si additives compared with such refractories containing Si powder.

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