Behavior of $ZrSiO_4$ in a reducing atmosphere

Dr. Z. A. Nemati; S. K. Sadrnezhaad, Dept. of Materials Science & Engineering – Sharif University of Technology, Tehran, Iran
B. Hashemi, Dept. of Materials Science & Engineering – Shiraz University, Shiraz, Iran

Abstract

Zirconia has several effects on the properties of composites and refractories. Adding of Zirconia might improve hydration resistance and/or corrosion resistance of the system, which is due to the conversion of CaO to $CaZrO_3$. However, high price of ZrO_2 is an important problem. Using cheaper materials such as zircon may be a suitable choice.

In this research, behavior of Zircon ($ZrSiO_4$) as a source of ZrO_2 has been investigated in a reducing atmosphere. For this purpose, mixtures of $ZrSiO_4$-Graphite and $ZrSiO_4$-MgO-C were heated at temperatures from 1000 °C to 1500 °C in a coke bed, and produced phases were analyzed and investigated by XRD, SEM and EDX.

The result showed that in the mixture of $ZrSiO_4$-Graphite, the zircon was disintegrated to ZrO_2 and SiO_2 in a reducing atmosphere at 1300 °C. Since, ZrO_2 is a stable phase at this condition; it appears as a monoclinic phase and/or tetragonal and monoclinic phases. Nevertheless, SiO_2 can precipitate as an amorphous phase or reduces to SiO (g) and reacts with carbon to form SiC or it may escape. In the mixture of $ZrSiO_4$-MgO-C, after heating at temperatures above 1300 °C, Zirconia and Forsterite ($2MgO.SiO_2$) were detected. The existence of these phases in the system was an indication that SiO_2 has reacted with MgO and confirmed disintegration of Zircon.

Introduction

Zirconia has several effects on the properties of composites and refractories, especially those systems containing CaO. Adding of Zirconia might improve hydration resistance of the system, which is due to conversion of CaO to $CaZrO_3$ [1-2]. The reaction involves with volume expansion that fills porosities and also, has melting point of 2400 °C. Therefore, in the systems containing CaO which are venerable to hydration, using of ZrO_2 as an additive may cause higher resistance to hydration of the refractory. From other hand, in the cement industries the studies have revealed that presence of ZrO_2 in refractories enhances corrosion resistance [3-5].

According to the studies, it has been shown that the presence of ZrO_2 in dolomite, magnesia-dolomite and magnesia – spinel refractories improves thermal shock resistance [5-7]. Tetragonal to monoclinic phase transformation of ZrO_2 and microcraking increases the toughness of refractories. However, high price of ZrO_2 is an important problem and limiting factor. Zircon ($ZrSiO_4$) is a source of ZrO_2. According to some references, zircon was disintegrated at 1676 °C, but the disintegration temperature depends on purity and atmosphere condition [8-9]. Zircon is a cheap material and is effective on sintering of ceramic bodies [10-11].

In this research, behavior of Zircon ($ZrSiO_4$) in a reducing atmosphere and effect of that on oxidation of MgO-C samples has been investigated. For this purpose mixtures of $ZrSiO_4$-graphite and $ZrSiO_4$-MgO-C were heated at temperature ranging from 1000 °C to 1500 °C in a coke bed and the produced phases were analyzed and investigated by XRD, SEM and EDX. Also oxidation resistance of samples containing 15% graphite with and without zircon was compared by measuring of oxidized layer thickness at temperatures from 1200 to 1500 °C.

Experimental Procedure

Zircon (Italian, 5 micron), magnesia (China, 0–5mm and 3.5 g/cm³) and graphite (China) with given compositions in **Tables 1-3** were used. Compositions of samples are given in **Table 4**. Samples ZS-G and ZS-M-G were made as 3 cm tablets. M-15G and M-15G-5ZS samples were made as cylinders with 3 cm diameter and 2.5 cm height. ZS-G and ZS-M-G samples were placed in a crucible and covered with coke and were heated from 1000 to 1550 °C for 5 hours.

MZ-15G and M-15G-5ZS samples were oxidized isothermally in controlled atmosphere from 1200–1500 °C. After that, the samples were heated to desired temperature in argon atmosphere, then heating continued in oxidized atmosphere (in oxygen) for one hour and then were cooled in argon atmosphere. Finally the samples were cut and thickness of oxidized layers was compared. Also cross section of samples and formed phases were investigated by SEM and EDX analysis.

Results and discussion

The XRD results of $ZrSiO_4$-G samples at temperatures from 1100 to 1400 °C are shown in **Figure 1**. $ZrSiO_4$ peaks are distinguishable up to 1200 °C, but at 1300 °C and above ZrO_2 and SiC peaks were appeared. These results indicate that $ZrSiO_4$ disintegrates to ZrO_2 and SiO_2 around 1300 °C and in reducing atmosphere. ZrO_2 is stable in reducing atmosphere and remain in mixture but SiO_2 could be reduced to SiO and react with carbon to produce SiC. The comparison of XRD diagrams at temperatures 1300–1400 °C with 1100–1200 °C and in 2 teta range of 22 to 30 degree shows that an amorphous phase (SiO_2) exist in mixture.

Figure 2 shows the XRD results of $ZrSiO_4$-MgO-G mixture at 1400 °C. The results indicated the formation of Mg_2SiO_4 and $MgSiO_3$

Tab. 1. Composition of China magnesia

Oxide	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	L.O.I
Percent	97.1	1.26	0.56	0.09	0.89	0.01

Tab. 2. Composition of zircon

Oxide	Percent
Al_2O_3	0.1
MgO	0.01
CaO	0.12
Fe_2O_3	0.06
TiO_2	0.12
SiO_2	34.02
Na_2O	0.01
K_2O	0.01
P_2O_5	2.0
ZrO_2+HfO_2	62.54
L.O.I	0.91

Tab. 3. Properties of graphite

Properties	Percent
Carbon	95.17
Moisture	0.02
Volatile materials	1.6
Ash	3.3
Density(gr/cm³)	2.26

Tab. 4. Composition of samples

Sample	% G	% ZrSiO4	% MgO
ZS-G	34	66	-
ZS-M-G	34.2	40.2	25.6
M-15G	15	-	85
M-15G-5ZS	15	5	80

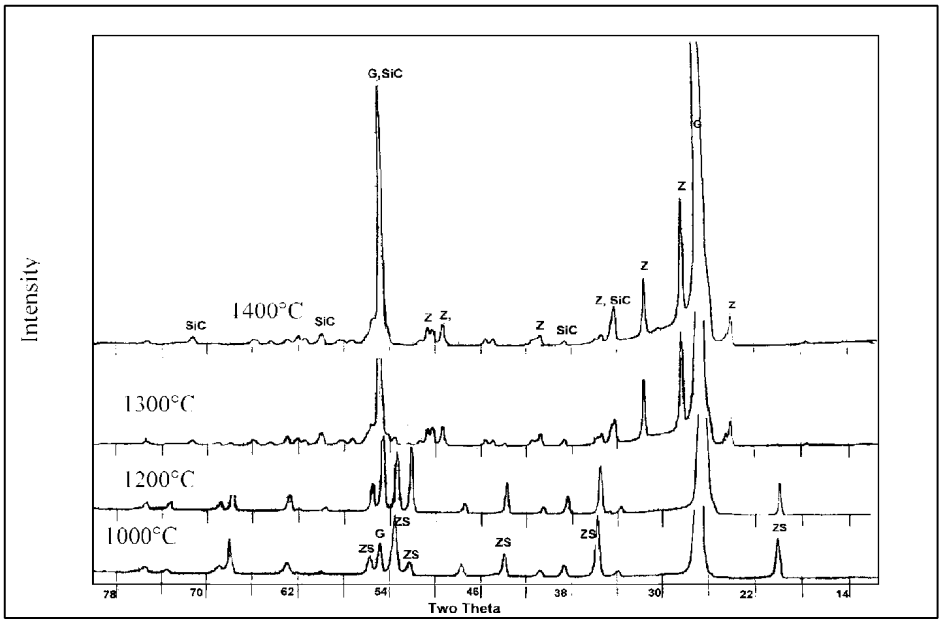

Fig. 1. XRD results of ZS-G samples after heating at different temperatures

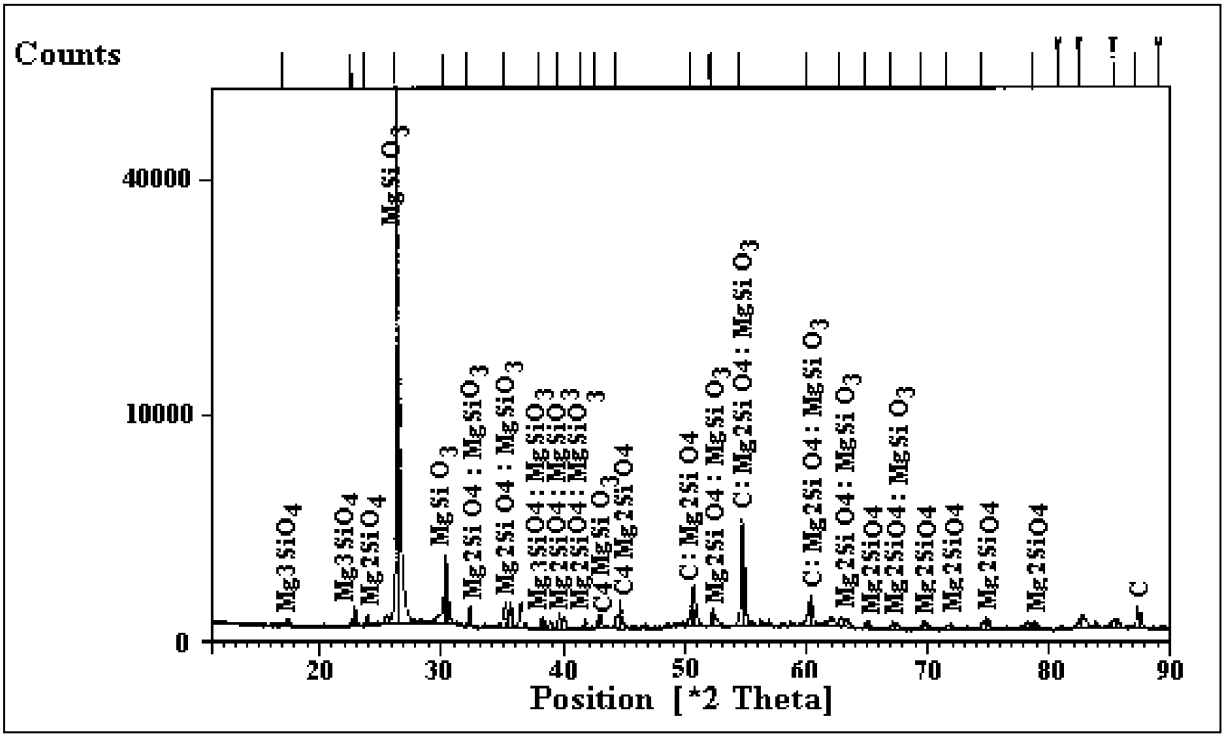

Fig. 2. The XRD result of sample ZS-M-G heated at 1400 °C

which meant that SiO_2 (from disintegration of $ZrSiO_4$) had reacted with MgO and produced mentioned phases according to following equations:

$SiO_2 + CO = SiO + CO$

$SiO + 2MgO + CO = Mg_2SiO_4 + C$

$SiO + MgO + CO = MgSiO_3 + C$

At temperatures above 1300 °C similar results were obtained. The SEM image of sample heated at 1300 °C and EDX analysis of different phases are presented in **Figures 3–4**. Small white particles are ZrO_2 grains and grey regions have Mg-Si composition.

Thickness of oxidized layer versus temperature for samples M-15G and M-15G-5ZS is shown in **Figure 5**. Oxidation of M-15G-5ZS samples is higher than M-15G, especially at 1500 °C. The SEM cross section image of MgO-C sample containing 15% G and 5% $ZrSiO_4$ is shown in **Figure 6**. EDX analysis shows that large particles are MgO with a narrow white-grey layer around it and small white particles are ZrO_2 particles. EDX analysis of narrow layer around the grains and grain boundaries near to surface of MgO particle are shown in **Figures 7 and 8** respectively. These analyses indicated that narrow layer contains Mg and Si and at grain boundary Ca-Si ratio is less than 1. Compositional change of MgO particle (with respect to original

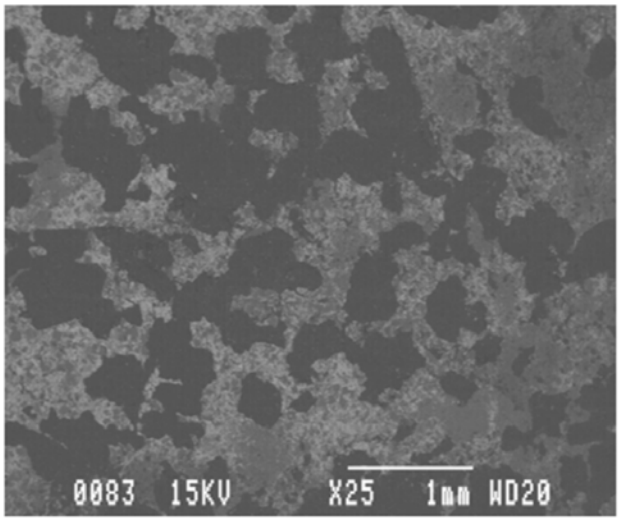

Fig. 3. SEM image of ZS-M-G sample heated at 1300 °C

composition) is due to disintegration of $ZrSiO_4$ and creation of ZrO_2 and SiO_2 or SiO (g). After that ZrO_2 has remained in texture, but SiO_2

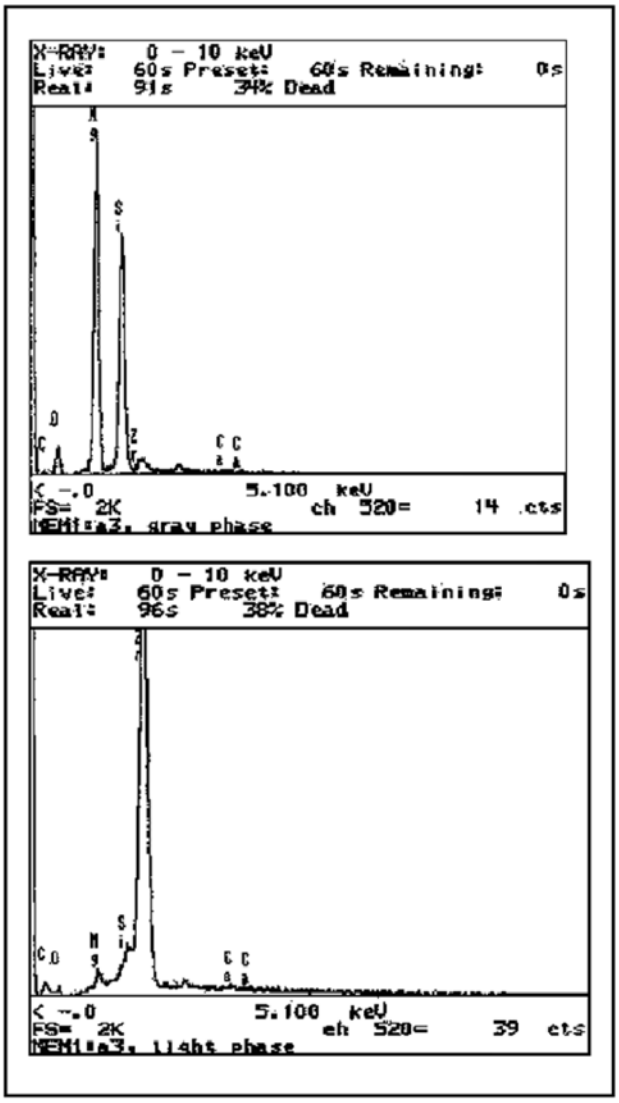

Fig. 4. EDX analysis of white and grey area in Fig. 3

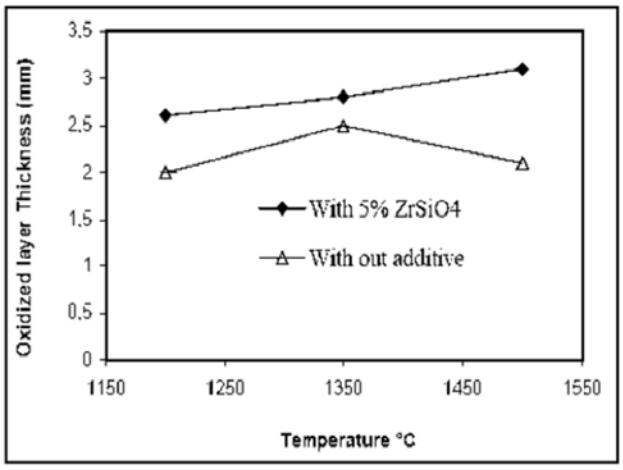

Fig. 5. Thickness of oxidized layer versus temperature

has reacted with surface MgO grain near the surface of ZrO_2 particle and created Forsterite. Our early analysis showed that adding of Zircon has increased porosity of samples. From other hand, the reaction of SiO_2 (resulting from zircon disintegration) with MgO grains surface inhibits and/or retards MgO reduction at high temperatures. So, it is possible that formation of dense layer on the sur-

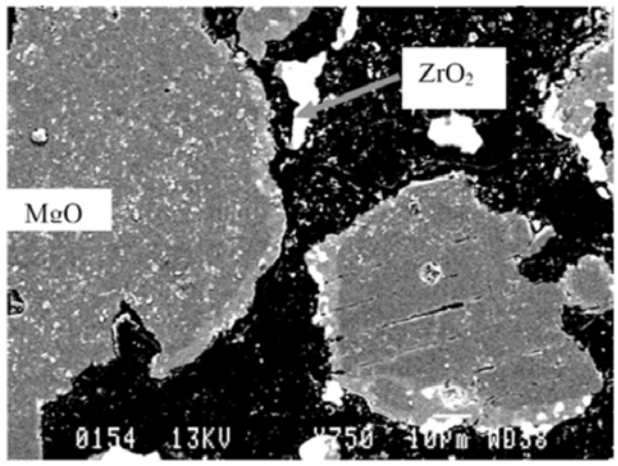

Fig. 6. SEM image from cross section of MgO-C samples containing $ZrSiO_4$

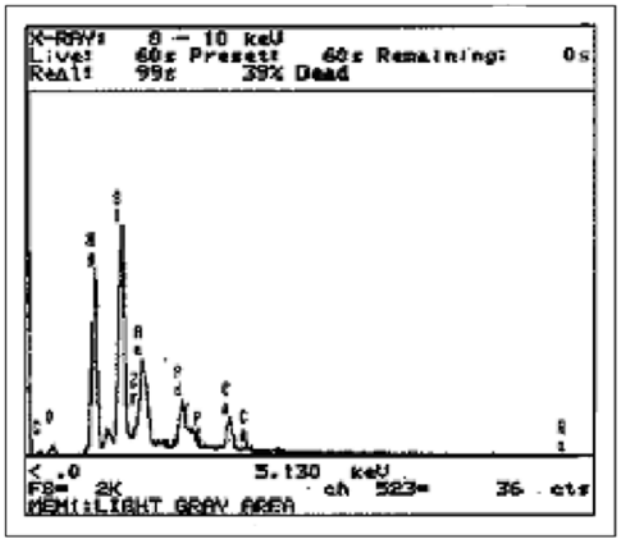

Fig. 7. EDX analysis of narrow white-grey region

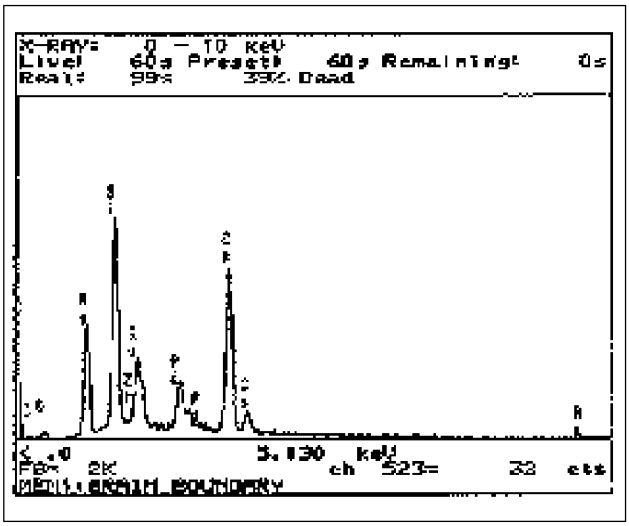

Fig. 8. EDX analysis of grain boundary near to surface of MgO grain

face of samples at high temperatures would be decreased. It seems to us that these would be possible reason that has been enhanced the oxidation in M-15G-5ZS samples.

Conclusions:

The result showed that $ZrSiO_4$ was disintegrated to ZrO_2 and SiO_2 in a reducing atmosphere at 1300 °C. Since, ZrO_2 is a stable phase in this condition; it appears as a monoclinic phase and/or monoclinic-tetragonal phase. Nevertheless, SiO_2 can precipitate as an amorphous phase or reduces to SiO (g) and reacts with carbon to form SiC. In the mixture of $ZrSiO_4$-MgO-C, after heating at temperatures above 1300 °C, Zirconia and Forsterite ($2MgO.SiO_2$) were detected. Existence of this phase in system indicated that SiO_2 reacted with MgO and confirms disintegration of Zircon. (F 37)

References

[1] D. J. Griffin, T. G. Miller: The Effect of Zirconia on Dolomite Refractories, Ceramic Transactions, Vol. 4, Advances in Refractories Technology, Ed. Robert E. Fisher, The American Ceramic Society, Inc. Westerville, Ohio, 1988, PP-360-374.

[2] H. Mollaie: Effect of ZrO_2 in Iranian dolomite in refractories application, Ph. D. Thesis, Iran University of Science and Technology, Tehran, Iran, 2002.

[3] H. Kozuka et al.: Further Improvements of MgO-CaO-ZrO_2 Bricks for Burning Zone of Rotary Cement Kiln, Unitecr 95, PP. 256-263.

[4] S. Radovanovic: The Reactions Between Zirconia From MgO-ZrO_2 Refractories and the Compounds of Portland Cement Clinker, Unitecr 95, P. 224, 1995.

[5] Z. Boguan, Q. Zhonigjun; H. Shihai: The Effects of Chemical Composition on Microstructure and Properties of MgO-CaO-ZrO_2 based Multiphase Materials, Proceedings of the Fourth International Symposium on Ref., Dalian, China, P. 289, 2003.

[6] S. P. Chaudhuri; N. C. Biswas and S. K. Patra: A Comparative Study of Dolomite and Dolomite-Zirconia Composite, Interceram, Vol. 51, No. 1, P. 42, 2002.

[7] V. C. Pandolfelli et al.; Evaluation of Thermomechanical Properties of Alumina Refractories Containing a Fused Mullite-Zirconia Aggregate, Unitecr 95, P. 373, 1995.

[8] S. Jialin, D. Shuiju: Influence of Various Zirconia Additives on High Temperature Properties of Magnesia Spinel Brick, Unitecr 95, P. 386, 1995.

[9] R. S. Pavlik; H. J. Holland: Thermal Decomposition of Zircon Refractories, J. Am. Ceram, Soc., 84 [12] 2930-36 (2001).

[10] M. Awaad; S. H. Kenawy: Sintering of Zircon: the Role of Additives, British Ceramic Transactions, 2003, Vol. 102, No. 2, P. 69.

[11] J. L. Rodriguez et al.: Reaction Sintering of Zircon-Dolomite Mixtures, Journal of the European Society 21 (2001) 343-354.

[12] C. Crabbe; J. J. Davies: Densification and Mineralogy of Alumina-Zircon Compacts, Br. Ceram. Trans. J. 88, 173-176, 1989.