

Development of Nitride-Bonded SiC Refractories by MgO and Nanocomposite (MgO/SiC) Additives

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In this study the microstructure and properties development of nitride bonded SiC refractories is reported in presence of MgO in laboratory and industrial scales. Also effect of nanocomposite addition (SiC+MgO) which synthesized by magnesiothermal process on optimized samples were studied.

The laboratory samples were prepared by mixing, shaping and firing at 1450–1600 °C in control atmosphere furnace. Phase analysis, microscopic observation and mechanical evaluation were taken as criteria for microstructure evolution. Also industrial samples were prepared by optimizing of firing cycle and additives. Then phase analysis, mechanical properties and inhomogeneity on properties of bricks in different part of muffle were investigated.

Variation of mechanical properties by using MgO additive could be attributed the microstructure evolution and mainly to liquid phase formation and grain morphology. It was found that the additives, such as MgO could modify the microstructure and influence the mechanical behavior. To extend results to industrial scale, settlement of bricks and modify firing cycle have been investigated to solve inhomogeneity problems. Finally, addition of nanocomposite (MgO+SiC) to optimized samples increased hot modulus of rupture (HMOR), which could be related to better sintering of matrix and formation of β -Si₃N₄.

1 Introduction

In recent years considerable attention has been devoted to development of nitride and oxynitride bonded SiC refractories [1–3]. Si₃N₄ bonded SiC is a high quality refractory with interesting mechanical and corrosion resistance properties for industrial applications [4]. Densification of Si₃N₄ bodies in solid state sintering, due to high directional feature of covalent bonding and its high vapor pressure at high temperatures is very difficult [5]. It has been claimed that the most effective method for improving the

densification of Si₃N₄ bodies, is the addition of metallic oxides [6–7]. In this method, the formation of SiAlON and liquid phase modifies the bonding system and enhances the evolution of a desired microstructure.

Microstructural development during the densification assisted by liquid phase is a function of type and amount of additives [8–9]. In order to optimize the mechanical properties of Si₃N₄ materials, it is necessary to know, the factors that affect the grain morphology and grain size during sintering process [10–11]. It has been well established that a nitride bond could provide improved high temperature properties [12]. The behavior of the nitride bonded refractories, however, is efficiently related to the amount of silicon and additives [13].

Results of the pervious papers showed that single and mixed additives such as Al₂O₃, MgO, Y₂O₃, Y₂O₃+ZrO₂, Al₂O₃+Y₂O₃, etc., are useful for enhancement of mechanical properties at high temperature [14]. Although the effect of Al₂O₃ and MgO addition to nitride bonded SiC ceramics have been studied to some extent, but need to modification to use in industrial scale .

N–SiC composed from two main component SiC grain and nitride bonding to increase high temperature mechanical properties. Many researchers used from nonoxide additives such as SiC and B₄C. Among nonorganic and inorganic materials, silicon carbide is an interesting compound. Silicon carbide is a suitable material in many applications due to its high toughness (29,1 GPa), low density (2,52 g/cm³), and high elastic modulus (448 GPa), being chemically neutral, high neutron, absorption thermoelectric properties and good antioxidant in MgO/C refractories [15]. In this regard, nanostructure of SiC with high surface area could be used as effective additive in N–SiC refractories.

One of the method to synthesize nanostructure SiC is the low temperature direct conversion of SiO₂/C nanocomposite structures by incorporated and mixing carbon from different sources. Kalbasi and Mosadegh [16] prepared poly(4-vinylpyridine) MCM-48 nanocomposites by in-situ polymerization of 4-vinylpyridine monomers inside the pores of MCM-48 silica. Low temperature reaction to prepare SiC can

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Keywords: N–SiC, nanocomposite, refractory

Tab. 1 Chemical composition of samples [mass %] [19]

Sample Additive	A	B	C	D	E	F	G	H
MgO	–	–	–	–	0,5	1	2	3
Al ₂ O ₃	–	–	–	–	–	–	–	–
Binder	–	–	–	–	3	3	3	3
Si	10	15	17,5	20	25	17,5	17,5	17,5

Tab. 2 Formulation of nanocomposites

Sample	I	J	K
C [mol]	1	2	2,5
SiO ₂ [mol]	1	1	1
Mg [mol]	2	2	2

be achieved by magnesiothermic reduction by using Mg. Shi, et al. [17] demonstrated the magnesiothermic reduction method for nanostructured SiC materials using a SiO₂/carbon nanocomposite as the precursor and Mg as the reducing agent at 600–900 °C. Zhao, et al. [18] synthesized mesoporous SiC by magnesiothermic reduction of a saccharose/SBA-15 composite at 650 °C. In this research, the attempt was to clarify the role of MgO in laboratory and industrial scales. Also it was tried to synthesise, nanocomposite (MgO/SiC) by a magnesiothermic process to be applied as an additive for N–SiC refractories. Results showed that using of nanocomposite (oxide, nonoxide) additives could be helpful to increase high temperature mechanical properties.

2 Experimental procedure

2.1 Experimental procedure in laboratory scale

The α-SiC powder with particle size below 1,25 μm was supplied by ESK-SiC GmbH/DE. The Si powder was metallurgical grade with average particle size of 15 μm. The chemical composition of samples is shown in Tab. 1. The MgO fine powder was an analytical grade. Different amounts of MgO were added to a base formula of 75 mass-% SiC and 25 mass-% Si [19]. Calciumlignosulphonate was used as a binder and mixing was carried out in a ball mill with polymer lining and zirconia balls. Cylindrical samples were produced by uniaxially pressing in a steel die at 150 MPa. Firing was carried out in a controlled atmosphere furnace at 1450–1600 °C under N₂ flow with a soaking time of 5 h [19]. To prepare MgO–SiC nanocomposites,

according to Tab. 2, firstly mesoporous MCM-48 was synthesized by dissolving 2,4 g hexadecyltrimethylammonium bromide in 50 ml deionized water and adding 50 ml ethanol and 12 ml of 32 mass-% ammonia. After mixing for 10 min, 3,4 g tetraethyl orthosilicate (TEOS) was added and mixed for 2 h at room temperature. The resulted solid products were filtered, washed with deionized water, dried at ambient temperature and calcined at 550 °C for about 5 h.

MCM-48/polyacrylamide nanocomposites were prepared by mixing 0,5 g of MCM-48 with a suitable amount of acrylamide monomer, benzoyl peroxide with 12 ml tetrahydrofuran in a round bottom flask. The mixtures were refluxed at 65–70 °C for 5 h and the result of MCM-48/polyacrylamide nanocomposites were filtered, washed with tetrahydrofuran and dried at room temperature. Mesoporous SiO₂/Carbon was then prepared from this MCM-48/polyacrylamide nanocomposite precursor by carbonizing in an Ar atmosphere at 700 °C at a heating rate of 5 °C/min and a holding time of 3 h. The resulted MCM-48/C nanocomposite was mixed with Mg powder in the molar ratio (SiO₂:Mg = 1:2) and heated in Ar at 550–600 °C at a heating rate of 5 °C/min and a soaking time of 6 h to synthesize mesoporous β-SiC. The product powder washed with distilled water and dried at room temperature [20].

Density, porosity and cold crushing strength (CCS) were measured according to DIN 51056 and DIN 51067. X-ray phase analysis was performed by using Cu and Co K_α radiation in a STOE-STADI-P diffractometer. Polished samples were examined by SEM/EDS Cambridge S-360 system at 10–20 keV.

For transmission electron microscopy (TEM), the bulk samples were ground to slices of 1 mm thickness. Three millimetre diameter discs ultrasonically drilled from the slices were mechanically ground and polished to around 80–100 μm, and then dimpled to 20 μm center thickness. These dimpled samples were Ar ion milled at 6 keV until perforation, coated with carbon, and examined in a Philips TEM 420/NL at 120 keV. Ordinary sample preparation have been done for TEM of powder sample and examined by (TEM, Zeiss EM10C/DE). Also to characterize powder sample, N₂ adsorption-desorption (BEL Inc-Belsorp/DE), differential scanning calorimetry (DSC, DSC-302, Bähr-Thermoanalyse GmbH/DE), and thermogravimetric analysis (TGA, Kimia Sanaat Ara, TG10) have been used.

2.2 Experimental procedure in industrial scale

In industrial scale, samples with similar formulation which optimized in laboratory scale were prepared. In this case, bricks with optimized formulation with dimension (10 cm × 12 cm × 60 cm) were prepared by pressing under 1500 kgf/cm². All bricks were put in SiC muffle. The muffle schematic, bricks settlement and firing cycle are shown in Fig. 1 a–c.

3. Result and discussion

3.1 Effect of Si content and firing temperature

Fig. 2 shows the density and porosity of the samples, which contain different amounts of Si and were fired at 1450 °C for 5 h. It is obvious, by increasing the amounts of Si in the primary batch, that the density of samples increases significantly to about 264 g/cm³ [21]. This could be attributed to nitride phase formation accompanied by a pore-filling effect [22]. The XRD patterns in (Fig. 3) show the evolution of different nitrogen-bearing phases with various amounts of silicon in the samples fired at 1450 °C for 5 h. Also it can be seen that the α to β–Si₃N₄ ratio increases with increasing silicon [23], while there is not any trace of Si or SiO₂ in samples fired over 1450 °C.

By XRD analysis (Fig. 3), the silicon oxynitride phase was identified, which could be related to the residual oxygen content in the firing atmosphere. By comparison of

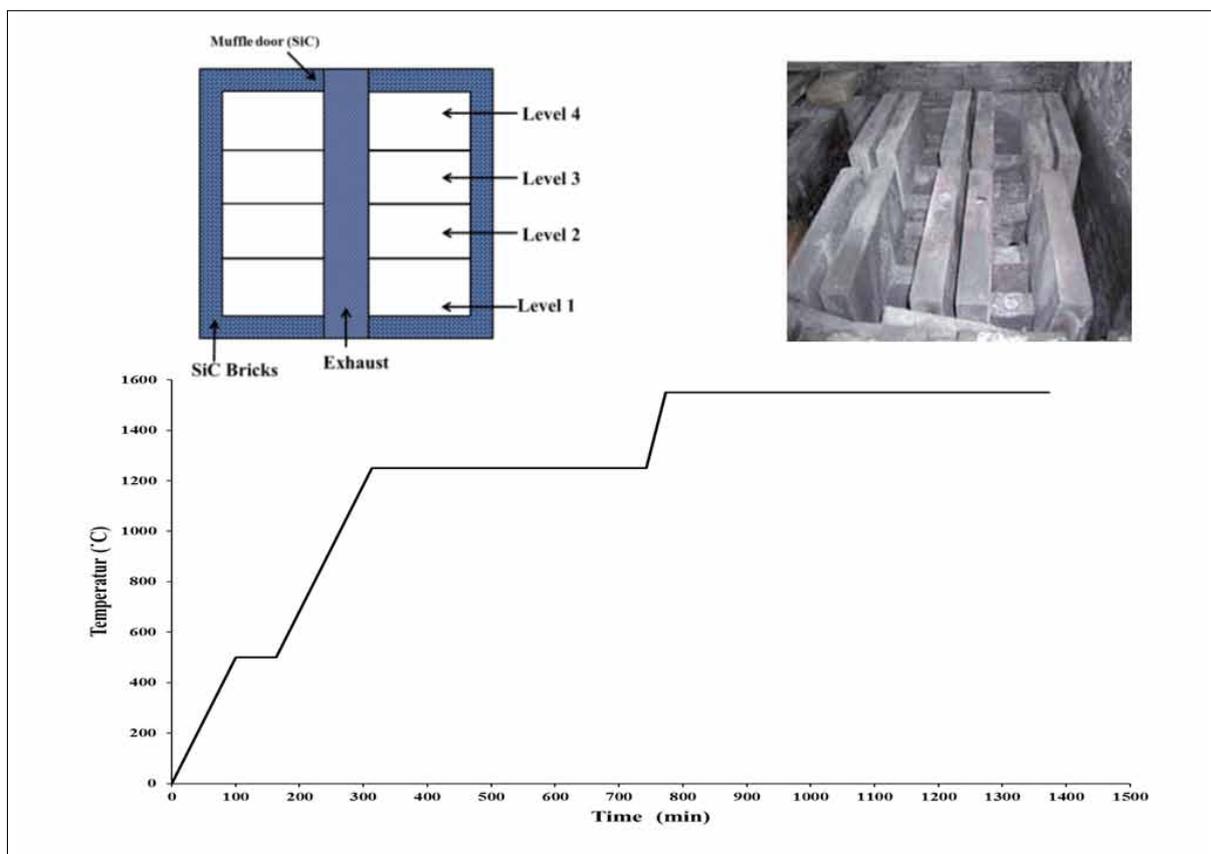


Fig. 1 a-c Schematic of muffle (a), settlement of bricks (b), and firing cycle (c)

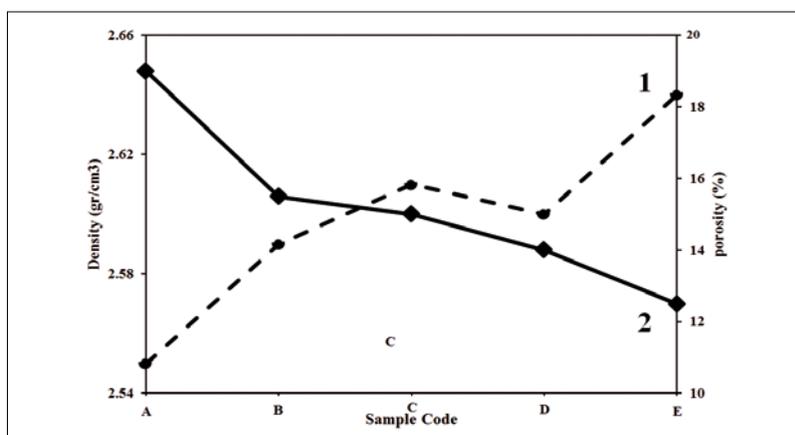


Fig. 2 Density and porosity of samples A–E fired at 1450 °C for 5 h: density (1), and porosity (2) [21]

mechanical and physical properties of sample E with others [12, 24, 25], this sample was selected.

In order to improve the properties of sample E, it was investigated the effect of increasing the firing temperature. The SEM micrograph of sample E is shown in Fig. 4. According to this figure, the formation of the liquid phase around the needle-shape nitride phase, and the α to β - Si_3N_4 phase transformation by

the solution-diffusion precipitation mechanism was improved [19]. By increasing the amount of Si (with iron impurity), the liquid phase is increased and then more β - Si_3N_4 phase is formed in the matrix, which brings almost an improvement of mechanical properties [19, 22].

The effect of firing temperature on the density and porosity of the samples is shown in Fig. 5. The optimum properties could

be reached at about 1550 °C, where the porosity is below 12 %. The increase of density up to 1550 °C could be related to grain growth of nitride phases and decreasing porosity. The slight decrease in density at higher firing temperatures could be attributed to nitride phase decomposition. By increasing both the amount of β - Si_3N_4 and the aspect ratio of this phase at higher firing temperatures [21], it was concluded that the aspect ratio and grain diameter have a strong effect on improvement of the mechanical properties, as was reported by Wötting [11]. According to above illustration, the formulation of sample C was selected, which fired at 1550 °C for further investigation the role of additives.

3.2 Effect of magnesia additive

The bulk densities of samples with different amounts of MgO were about 2,57–2,67 g/cm³ depending on firing temperatures. Density is improved with increasing temperature from 1500 °C to 1600 °C. The density of samples doped with 0,5–3 mass-% MgO and fired at 1500 °C for 5 h is almost the same as that of samples

without any additive fired at 1550 °C for 5 h. This indicates that the addition of MgO initiates the formation of liquid phase via reaction with silica layer existing on SiC particles. This was supported by EDS of liquid phase, which revealed Ca, Si and Mg. The ternary diagram of CaO–MgO–SiO₂ shows that the formation of liquid phase can happen at 1400 °C [26].

The presence of CaO in the liquid phase is attributed to the use of calcium-lignosulphonate binder. Variation of cold crushing strength with different amounts of MgO is shown in Fig. 6. By addition of MgO of 0,5–3 mass-% the CCS is decreased from 160 MPa to about 120 MPa at 1550 °C. In spite of the variation in CCS values, the density of samples at different temperatures with addition of different amounts of MgO did not show any significant changes. This behavior could be attributed to the fact that the mechanical strength is related to morphology of nitride phases [21]. The nature of liquid phase affects not only the viscosity but also the morphology of β-Si₃N₄ grains. The formation of β-Si₃N₄ and liquid phases was confirmed by TEM observations. The TEM image (Fig. 7) shows the formation of nitride phases following the solution-diffusion-precipitation (SDP) mechanism. The XRD results of samples containing 0,5 and 2 mass-% of MgO respectively are shown in Fig. 8. This as reported before indicates that the liquid phase has a dominant role in the formation of β-Si₃N₄ phase [24].

Fig. 9 shows the SEM micrographs of samples containing 0,5 and 2 mass-% MgO respectively and the slight grain size difference of nitride phase due to an increase in MgO amount can be observed. Several microscopical observations clarified that the grain texture mainly influenced in terms of width to length ratio. MgO as a strong modifier reduces viscosity in silicate based glasses [27]. It seems that during reduction of viscosity by addition of MgO, both nucleation and grain growth are improved. This influence on grain morphology (aspect ratio and grain diameter) is in line with literature [9]. Probably local super saturation, which is related to kinetic parameters of the liquid phase such as viscosity, affects the morphology of nitride phases and finally influences mechanical properties. In other words, the mechanical property variation is more affected by the grain aspect ratio as by the grain size

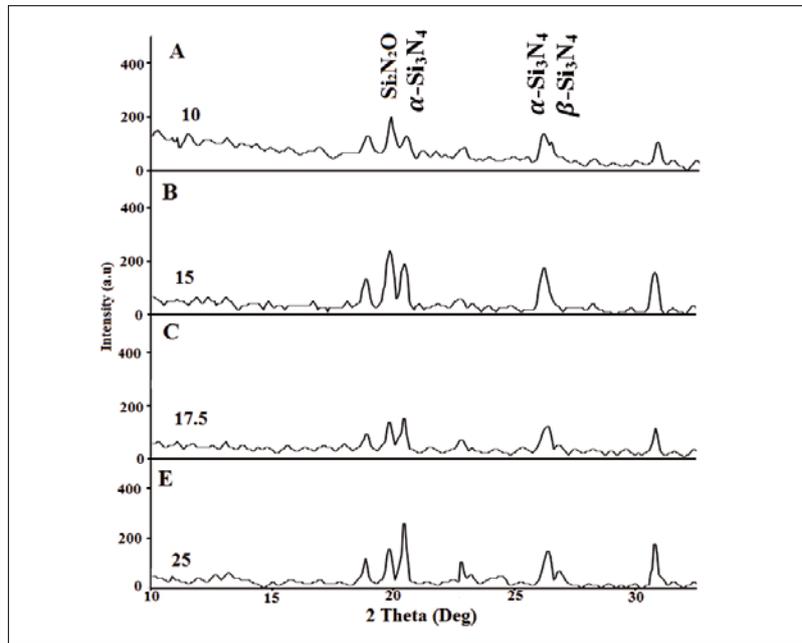


Fig. 3 XRD patterns of samples A–E fired at 1450 °C

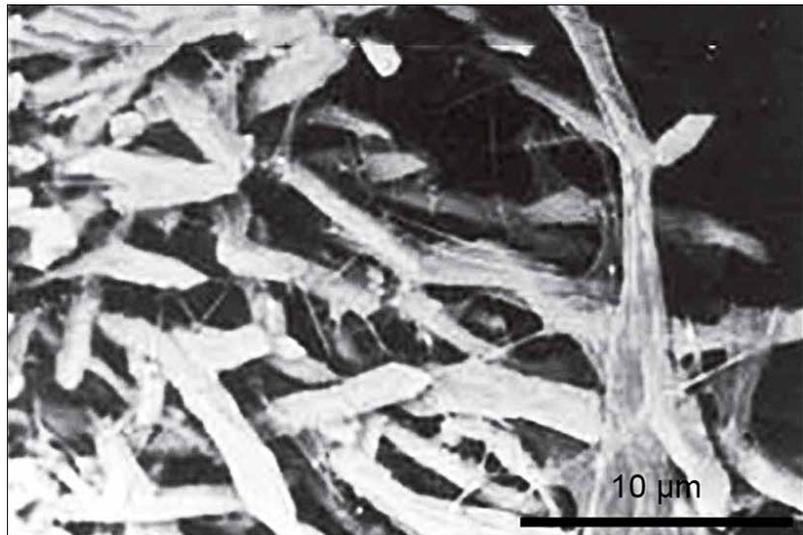


Fig. 4 SEM image of sample E fired at 1450 °C for 5 h [21]

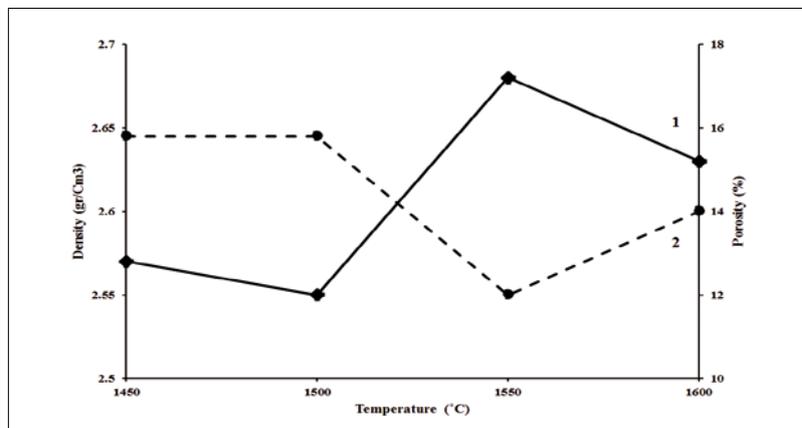


Fig. 5 Density (1) and porosity (2) of sample E fired at different temperatures [21]

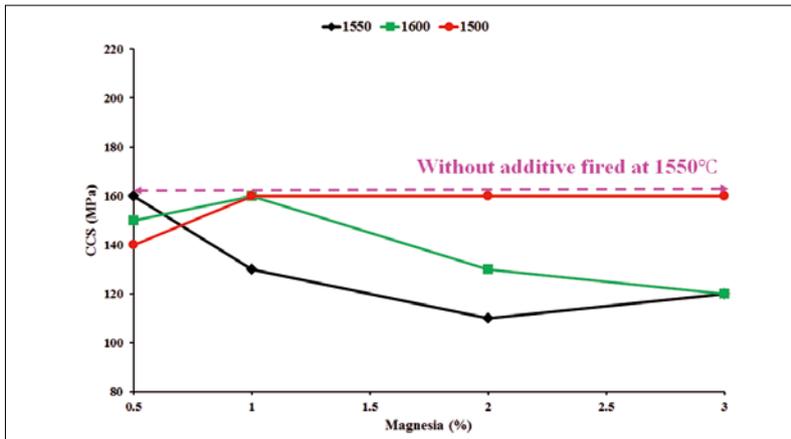


Fig. 6 CCS vs. various amounts of MgO

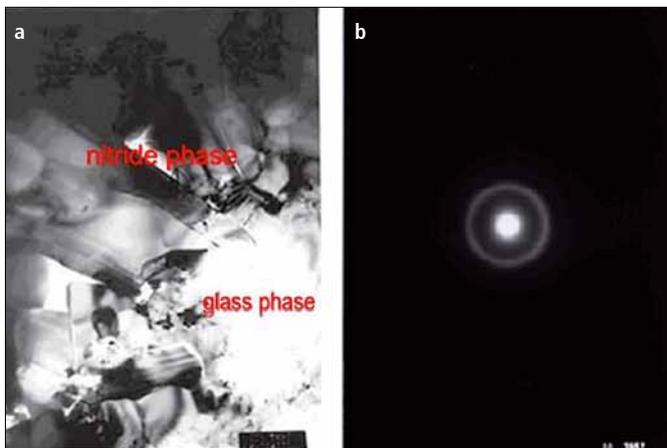


Fig. 7a–b TEM image of sample G (a) and diffraction pattern of glassy phases (b)

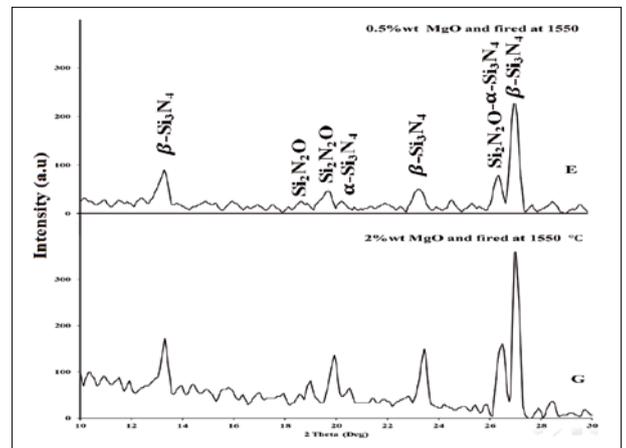


Fig. 8 XRD patterns of samples containing 0,5 and 2 mass-% MgO respectively, and fired at 1550 °C for 5 h

itself. Moreover, the strength decrease also can be attributed to the mismatch expansion nature of liquid and crystal phases. This may initiate the primary cracks in the matrix and decrease the CCS [19].

3.3 Effect of nanocomposite additive

XRD results (Fig. 10) show that when the stoichiometric amount of Mg is used, no

SiO₂ remains and complete reduction occurs, but Mg₂Si is formed, suggesting the presence of extra Mg [28].

X-ray diffraction patterns of the carbonized mixtures of polyacrylamide/MCM-48 nanocomposite with Mg in the different molar ratios of C:SiO₂:Mg (sample I to K), heated at 550–600 °C for 6 h. Each of the samples of the three molar compositions before acid etching (Fig. 10a) contains β-SiC. As the carbon content is increased, the contact distance between the SiO₂ and Mg is increased by dilution with the carbon in the mixture, and therefore causes a decrease of the diffraction peak intensity of the

β-SiC product. The XRD patterns of the acid leached samples (Fig. 10b) contain only the (111), (220) and (311) reflections of cubic β-SiC and no evidence of Mg₂Si, Mg₂SiO₄ or carbon.

Fig. 11a–b present TEM images of mesoporous SiC in the temperature range 550–600 °C showing SiC particles of about 230 nm in diameter.

From above results it was decided to use from stoichiometric ratio C:SiO₂:Mg = 1:1:2 (sample I) [20]. This microstructure could be useful for sintering of SiC particle in matrix. Properties of samples containing MgO and nanocomposite additives (1 mass-% MgO and 2 mass-% SiC–MgO) were investigated and results observed in Tab. 3. In Tab. 3 there is sharp increase in HMOR could be seen which was found between 50–55 MPa. This phenomenon could be related to better sintering of matrix and lower amount of liquid phase.

Tab. 3 Physical and mechanical properties of samples

Sample	Density [g/Cm ³]	Prosity [%]	CCS [MPa]	HMOR [MPa]	TEC [1/°C]
1 mass-% MgO	2,66	13	193	30–35	4,1 × 10 ⁻⁶
2 mass-% SiC+MgO nanocomposite	2,7	10	245	50–55	4 × 10 ⁻⁶

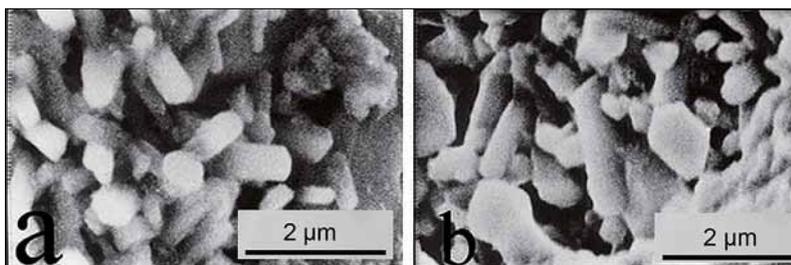


Fig. 9 SEM micrographs of samples containing: a) 0,5 mass-% MgO, and b) 2 mass-% MgO

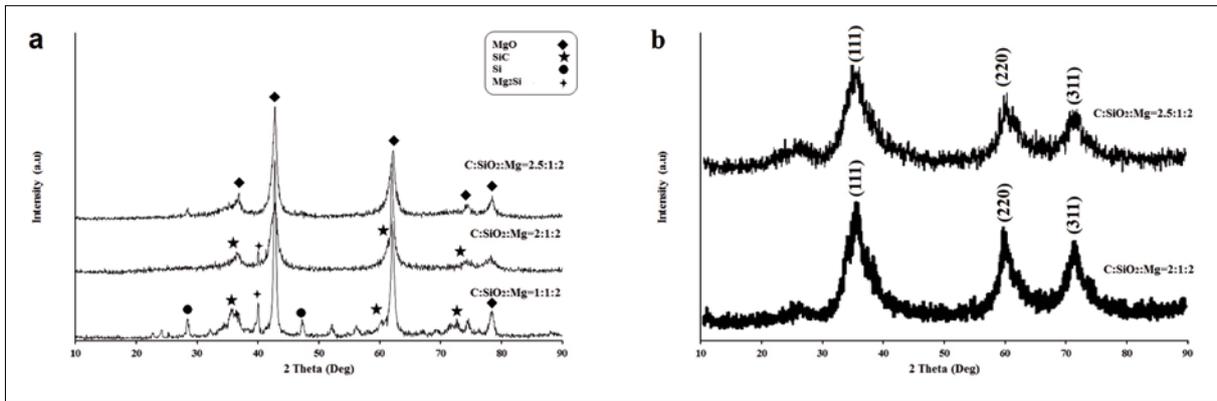


Fig. 10 X-ray diffraction pattern of mesoporous β -SiC synthesized at 550–600 °C: **a)** before acid etching, and **b)** after acid etching

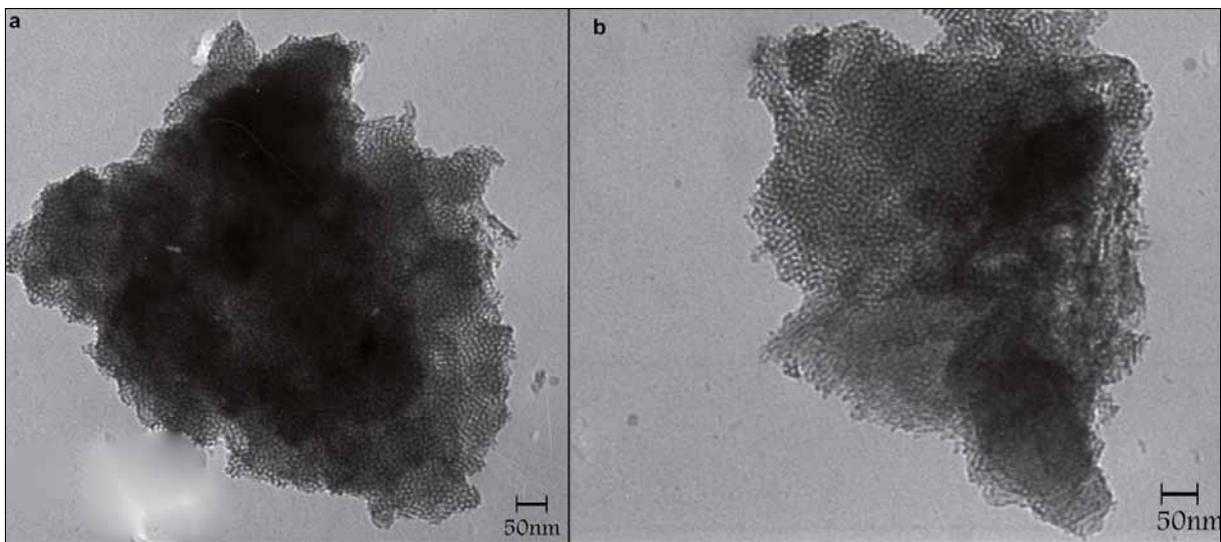


Fig. 11 TEM images of synthesized mesoporous SiC in temperature range 550–600 °C: **a)** 63 000x, and **b)** 100 000x

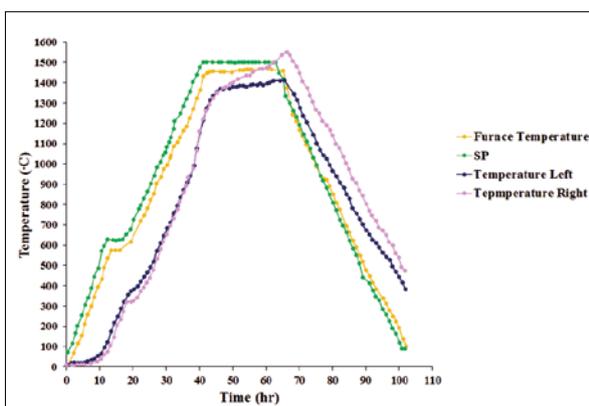


Fig. 12 Firing cycle, set point (SP), left part of the muffle, and right part of the muffle

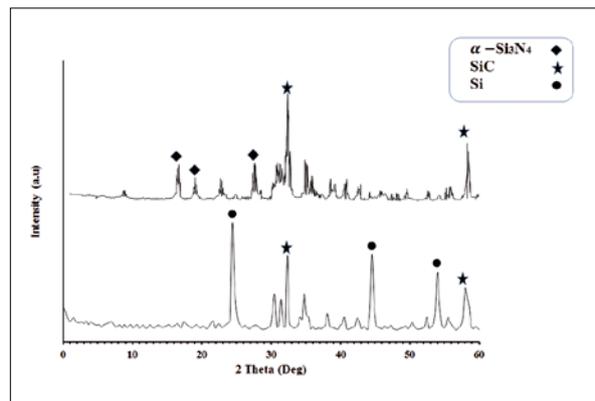


Fig.13 XRD pattern of sample: **a)** first firing, and **b)** ninth firing (revised firing cycle)

In spite of the important role of additives which illustrated above to extend these results to industrial scale, inhomogeneity on properties must be considered for samples which put in different part of muffle.

3.5 Solving of inhomogeneity properties for sample in industrial scale

Because of inhomogeneity of properties of samples that put in different parts of muf-

file, the bricks were arranged in a way that the gas is spread, evenly all throughout the muffle Fig. 1b. Also to solve inhomogeneity problems there were optimized the firing curve, soaking time, different steps during

firing curve and the N_2 flow through the muffle (Fig 12).

Fig. 13 shows the XRD pattern of samples which were put in level one at different firings (first and ninth). After revising the process, there could not be observed any Si residual remain in the brick.

4 Conclusion

The addition of MgO, Al_2O_3 and nanocomposite (MgO–SiC) to nitride bonded refractories in laboratory and industrial scale have been investigated and results showed that :

1. In samples containing magnesia as an additive, the mechanical variation is more affected by the grain aspect ratio than the grain size itself.
2. The strength decrease can be attributed to the mismatch of expansion coefficients of liquid and crystal phase as well as changes on aspect ratio of needlelike nitride phase.
3. The silicon amount and firing temperature have a great influence on the formation of nitrogen-containing phases in Si_3N_4 -bonded SiC refractories.
4. Nanocomposite MgO/SiC had a positive role to develop of high temperature mechanical properties (HMOR) of N–SiC refractories. Also the presence of SiC and MgO in nanocomposite (MgO/SiC) could be useful for α to β transformation and also better sintering of SiC in N–SiC refractories.
5. In industrial scale, to get suitable results, the inhomogeneity on properties must be solved by considering the firing curve, soaking time, different steps during firing and by optimizing the N_2 flow.

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