SYNTHESIS OF $MgAl_2O_4$-Ti(C,N) NANOCOMPOSITE BY ALUMINOTHERMIC REDUCTION

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Abstract: *$MgAl_2O_4$/Ti(C,N) composites were synthesized through aluminothermic reaction between Al,TiO_2,MgO powders and phenolic resin in coke bed condition. Effect of addition of carbon black and sugar into the mixture at different temperatures were investigated. The phases and microstructures of samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). $MgAl_2O_4$/Ti(C,N) composites without additive were obtained after heat treatment at 1600˚C. With addition of carbon black TiC, TiN and Ti(C,N) were appeared after firing at 1400˚C and formation of spinel/Ti(C,N) composites were completed at 1600˚C. In sample containing sugar, $MgAl_2O_4$-Ti(C,N) composite were completely synthesized at 1400˚C. In this sample crystallite size of Ti(C,N) were 32 nm and carbon content of titanium carbonitride (Ti(C,N)) reached to 0.442 value.*

Keywords: *$MgAl_2O_4$-Ti(C,N) composite; Aluminothermic reaction; Coke bed, TiC, TiN, Spinel*

1. INTRODUCTION

Magnesium aluminate spinel ($MgAl_2O_4$) is a well known refractory material in the steel ladles and cement rotary kilns because of it's attractive properties such as high melting point (2135˚C), high thermal shock resistance, high chemical inertness and low thermal expansion coefficient [1, 2].Titanium carbide (TiC) with cubic structure of NaCl is an important ceramic materials due to its high hardness (28 GPa), good thermal conductivity (21 W/m^2.k), high melting point (3065˚C) and high resistance to oxidation and corrosion [3-5]. Titanium nitride (TiN) attracted great interest for many structural and coating applications due to its high melting temperature (2950˚C), high Vickers hardness (21 GPa) and good corrosion resistance to acidic slag and alkaline slag [5-7]. $MgAl_2O_4$/Ti(C,N) composite have good properties and potential application for used in steel and aluminium industry. In refractories containing carbon such as MgO-Al_2O_3-C with addition of TiO2, $MgAl_2O_4$-Ti(C,N) in situ establish at high temperature and improve the corrosion and oxidation resistance of refractory [8].

Many novel methods have been developed over the last decades for the synthesis of ceramic and composite powders such as sol-gel method, hydrothermal processing, combustion route and molten salt synthesis [9]. In comparison with normal synthesis routes such as firing of mixed oxides at high temperature, these novel methods are small scale production and give high purity, controlled shape and size of particles [10]. For synthesis of TiC, many methods such as carbothermal reduction of TiO_2 powders using carbon, self propagating high temperature synthesis (SHS) direct reaction between the Ti metal and carbon have been developed [11]. For synthesis of TiN, directly reacting metallic Ti with nitrogen gas, SHS and solid-state metathesis reactions were developed [12]. In some of these methods, some additives assist to formation of carbides and nitrides from oxides raw materials. In synthesis of TiN raw materials such as TiO_2, NaN_3, Mg, Na, sulfur were mixed and put into autoclave at 150˚C for 2h. In this procedure, exothermic reaction of Na and S and reducing action of Mg, accelerated the formation of TiN at low temperatures [13].

In this article, $MgAl_2O_4$/Ti(C,N) composite was produced by aluminothermic reduction in coke powder bed condition, and the effect of addition of carbon black and sugar into mixture at different temperatures were investigated.

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2. EXPERIMENTAL PROCEDURES

The starting materials were aluminium powder (Merck, 99% purity), titanium oxide (anatase, Merck, 98.5% purity), MgO (Merck, 99.5% purity), carbon black from Iran carbon Co. (98.5% purity, <73 μm) and novalak resin. Average particle sizes were measured to be 88 μm for aluminium powder, 1.8 μm for TiO_2 and 9.18 μm for MgO. Aluminium, titanium oxide and magnesia were weighted according to the stoichiometry of reactants in Eq. (1)[14] and then they were mixed with resin as carbon source to form anticipated products. Novalak resin yields 55Wt.% carbon after tempering at above 200˚C.

$$8Al + 6TiO_2 + xMgO + 3N_2 + 6C = xMgAl_2O_4 + (4-x)\,Al_2O_3 + 6Ti(C,N) \quad (1)$$

Three type of powder mixtures were prepared: (i) A stoichiometric mixture termed EB; (ii) A stoichiometric mixture + 10% addition of carbon black termed EC; (iii)A stoichiometric mixture + 30% addition of sugar solution termed ES. For preparing of ES mixture,TiO_2 powder was added to 30% aqueous sugar solution, refluxing was performed for 5h at 120 ˚C and then stoichiometric amounts of MgO and Al powder was added and finally mixture was heated at 300 ˚C for 3h. With this route the dry homogeneous mix powder with carbon that yield from sugar was obtained.

EB, EC and ES formula were mixed with novalak resin as a binder. Three mixtures were aged for 24h in atmospheric condition and then were pressed with uniaxial press (30 MPa final pressure) into pellet shapes with 10mm diameter. After curing the pellets at 200˚C/24h, they were heat treated in an electrical furnace with a rate of 10˚C/min at 1200-1600˚C with 3 h soaking time.

The X-ray diffraction patterns of samples were obtained using Philips X-ray diffractometer (Model PW3710) with CuKα radiation. The Microstructure of samples were characterized by scanning electron microscopy (SEM, VEGAIIXMU).

The crystallite size ‘D(nm)’ was determined from X-ray line broadening using the Scherer formula:

$$D = 0.9\lambda/B\cos\theta \quad (2)$$

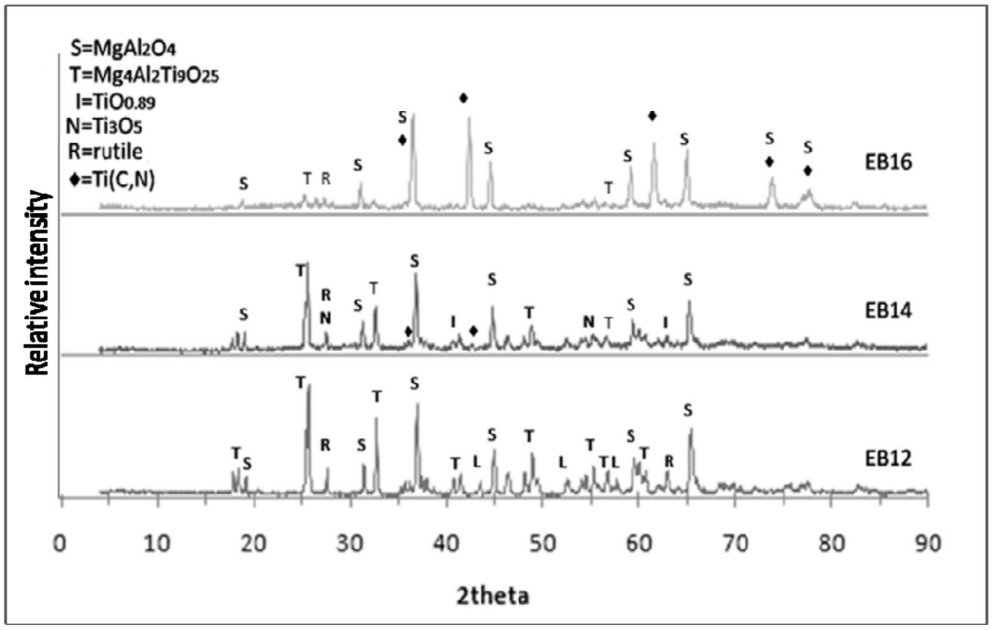

Fig.1. XRD patterns of EB samples after synthesized at 1200˚C (EB12), 1400˚C (EB14) and 1600˚C (EB16)

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Where 'D' is the crystallite size, B is the full width at half of the maximum intensity, λ is the wavelength of the X-ray radiation and θ is the Bragg's angle. Line broadening due to the equipment was subtracted from the peak width before calculating the crystallite size.

3. RESULTS AND DISCUSSION

3.1. Phase Evolution in Samples Without Additives

Fig. 1 shows the XRD patterns of samples without additive (EB) heated at different temperatures (1200-1600˚C). $MgAl_2O_4$ (MA) and $Mg_4Al_2Ti_9O_{25}$ (MAT) were main phases at 1200˚C. Ti_3O_5 and TiO_{2-x} peaks which were titanium oxide with lower degree of oxygen were appeared at 1400˚C from reduction of rutile. At 1400˚C some of Ti(C,N) peaks were appeared but formation of Ti(C,N) phase were completed at 1600˚C.

The consideration system were MgO, Al,TiO_2 and C. Carbon were residual from resin. Under coke powder bed condition CO and N_2 gases were existed with partial pressure of 3.5×10^4 Pa for CO(g) and 6.5×10^4 Pa for N_2(g) [15]. During heat treatment of Al, TiO_2, MgO and carbon, once the temperature exceeds from the melting point of Al (660 ˚C), molten Al spreads with capillary tube suction between other particles such as TiO_2, carbon and MgO. TiO_2 particles reduce to suboxides of titanium such as Ti_3O_4, TiO_{2-x} and Al converted to Al_2O_3. Residue carbon from resin and CO(g) from burning of coke also reduce TiO_2. With present of N_2(g), TiO_xN_y also established from solution of nitrogen atoms in Ti_3O_5 or other suboxides of titanium oxide [15]. Then TiO_xN_y with CO(g) or other reducing agent converted to TiN or Ti(C,N). According to MgO-Al_2O_3-TiO_2 phase diagram (Fig. 2) Al_2TiO_5 and $MgTi_2O_5$ with pseudobrookite structure completely dissolve in each other and establish MAT phase that observed in EB sample at different temperatures.

The formation of $MgTi_2O_5$ is reported by Yuanbing [6] in 8Al-TiO_2-4MgO mixtures after firing at 1400˚C for1h at N_2 atmosphere. In this study in reduction atmosphere, MA spinel is more stable than solid solution of $MgTi_2O_5$-Al_2TiO_5, therefore MAT may decompose according to following reaction:

$$Mg4Al_2Ti_9O_{25} \rightarrow MgAl_2O_4 + Mg_2TiO_4 + MgO + 8TiO_2$$

Mg_2TiO_4 has spinel structure with complete solubility with $MgAl_2O_4$ (Fig. 2). MgO may react with Al_2O_3 which formed from reduction of TiO_2 by Al and established additional spinel solid solution.

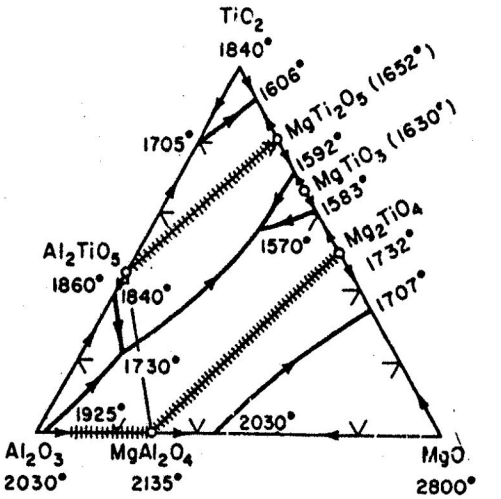

Fig. 2. phase diagram of Al_2O_3-MgO-TiO_2

3. 2. Addition of Carbon Black

Fig.3 shows XRD patterns of powder samples with addition of carbon black (EC) after firing at 1200, 1400, 1600˚C. MA spinel, MAT, rutile and titanium suboxides phases were identified after heating at 1200˚C. With increasing temperature up to 1400 ˚C, the relative intensity peaks of MAT were decreased slightly due to decomposition to solid solution of spinels and TiC, TiN and Ti(C,N) peaks were appeared. As the temperature exceeds to 1600˚C, Ti(C,N) and MA spinel phases were main phases. Using carbon black caused to formation of TiC after firing at 1400˚C and then converted to Ti(C,N) at 1600˚C. Carbon has a main role to reduction of TiO_2 and provides carbothermal reduction of

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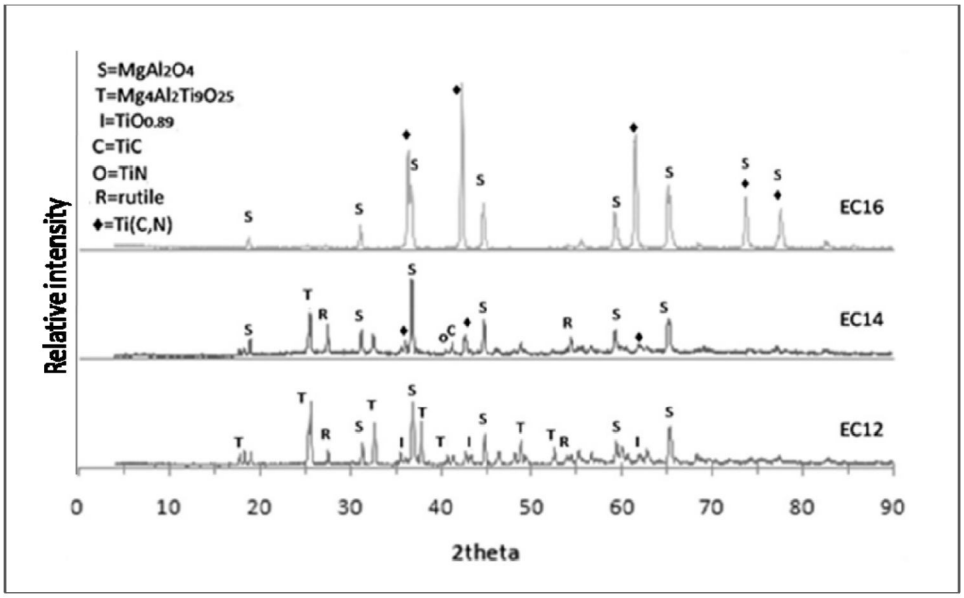

Fig. 3. XRD patterns of EC samples after synthesized at 1200˚C (EC12), 1400˚C (EC14) and 1600˚C (EC16)

TiO_2 as following reaction [11]:

$$4TiO_2(s) + C(s) \rightarrow Ti_4O_7(s) + CO(s) \quad (3)$$
$$3Ti_4O_7(s) + C(s) \rightarrow Ti_3O_5(s) + CO(g) \quad (4)$$
$$Ti_3O_5(s) + 8C(s) \rightarrow 3TiC(s) + 5CO(g) \quad (5)$$

Continuous transformation of CO and CO_2 into each other according to following reaction occurred in these three stages:

$$2CO = C + CO_2 \quad (6)$$

3. 3. Addition of Sugar

Fig.4 shows XRD patterns of samples with addition of sugar (ES) after firing at 1200, 1300, 1400 ˚C. According to XRD patterns, synthesis temperature of $MgAl_2O_4$-Ti(C,N) composite decreased to 1400˚C with addition of sugar which associated with high surface area of carbon residue from sugar and its homogeneous dispersion. The reason for this larger surface area may be related to the finer particle size of in situ carbon formation during sugar tempering. In addition, in prepared samples,sugar solution (30% in water) and TiO_2 were blended together; hence it was presumed that the TiO_2 particles were covered by sugar solution that then was transformated to carbon. Hence reaction between the TiO_2 and C were accelerated and formation of Ti(C,N) was occurred at 1400˚C .

Crystallite size of Ti(C,N) was calculated from XRD pattern of samples and results listed in Table 1. As seen in Table 1 crystallite size of

Table 1. Crystallite size of Ti(C,N) prepared by aluminothermic reduction at 1400 and 1600˚C for 3h.

Sample and its code	Temperature (˚C)	Crystallite size of Ti(C,N) (nm)	Crystallite size of $MgAl_2O_4$ spinel(nm)
EB	1600	35.840	29.843
EC	1600	45.103	41.103
ES	1400	32.756	33.870

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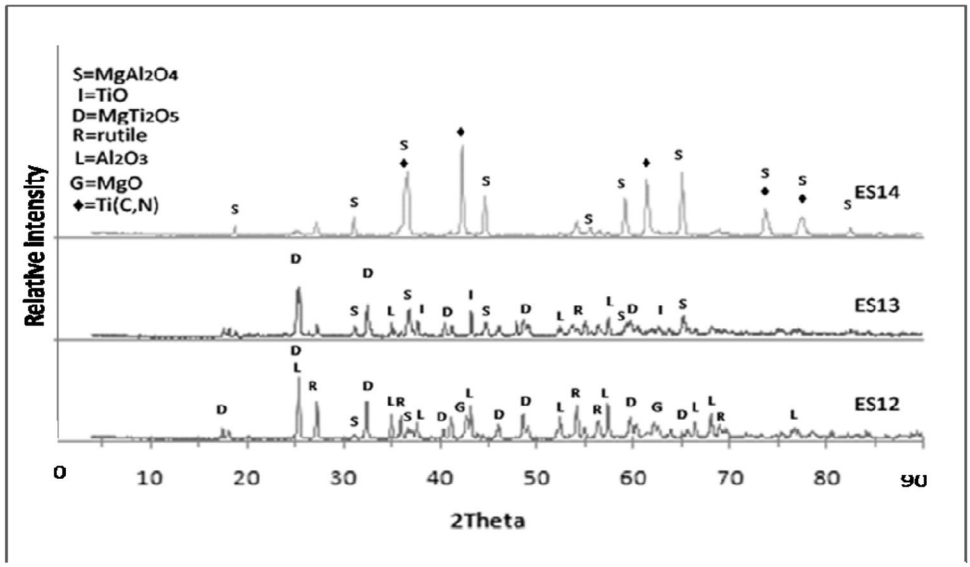

Fig. 4. XRD patterns of ES samples after synthesized at 1200˚C (ES12), 1300˚C (ES13) and 1400˚C (ES14).

Ti(C,N) formed in all samples are nano crystallites. It seems that addition of sugar (ES formula) has a significant influence on the crystallite size of Ti(C,N) which it is decreased to 32.7 nm.

Lattice parameters of $Ti(C_x,N_{1-x})$ as a function of C contents are written as follows [6]:

$$a = 0.4235 + 0.007x \text{ (nm)} \quad (7)$$

Where a is lattice parameter of $Ti(C_x,N_{1-x})$ and x is C content in $Ti(C_x,N_{1-x})$, that were obtained from above formula.

The results of carbon contents in different samples according to Table 2 show that with addition of carbon black and specially sugar to the powder mix, the amounts of C contents in $Ti(C_x,N_{1-x})$ were increased and reached to 0.442 after firing of ES sample at 1400˚C.

3. 4. The Microstructure Analysis

Microstructure of composites were studied by SEM, using back scattered electron image (BSE) mode coupled with EDS (energy dispersive spectroscopy). In this study only metallic constitutes of each sample were measured since carbon and nitrogen contents cannot be

Table 2. Lattice parameter and Carbon value of Ti(C,N) prepared by aluminothrmic reduction at different temperatures for 3h.

Sample and its code	Temperature (˚C)	Lattice parameter of $Ti(C_x,N_{1-x})$ (nm)	Carbon value in $Ti(C_xN_{1-x})$
EB	1600	0.4255	0.028
EC	1400	0.4257	0.314
	1600	0.4260	0.357
ES	1400	0.4279	0.442

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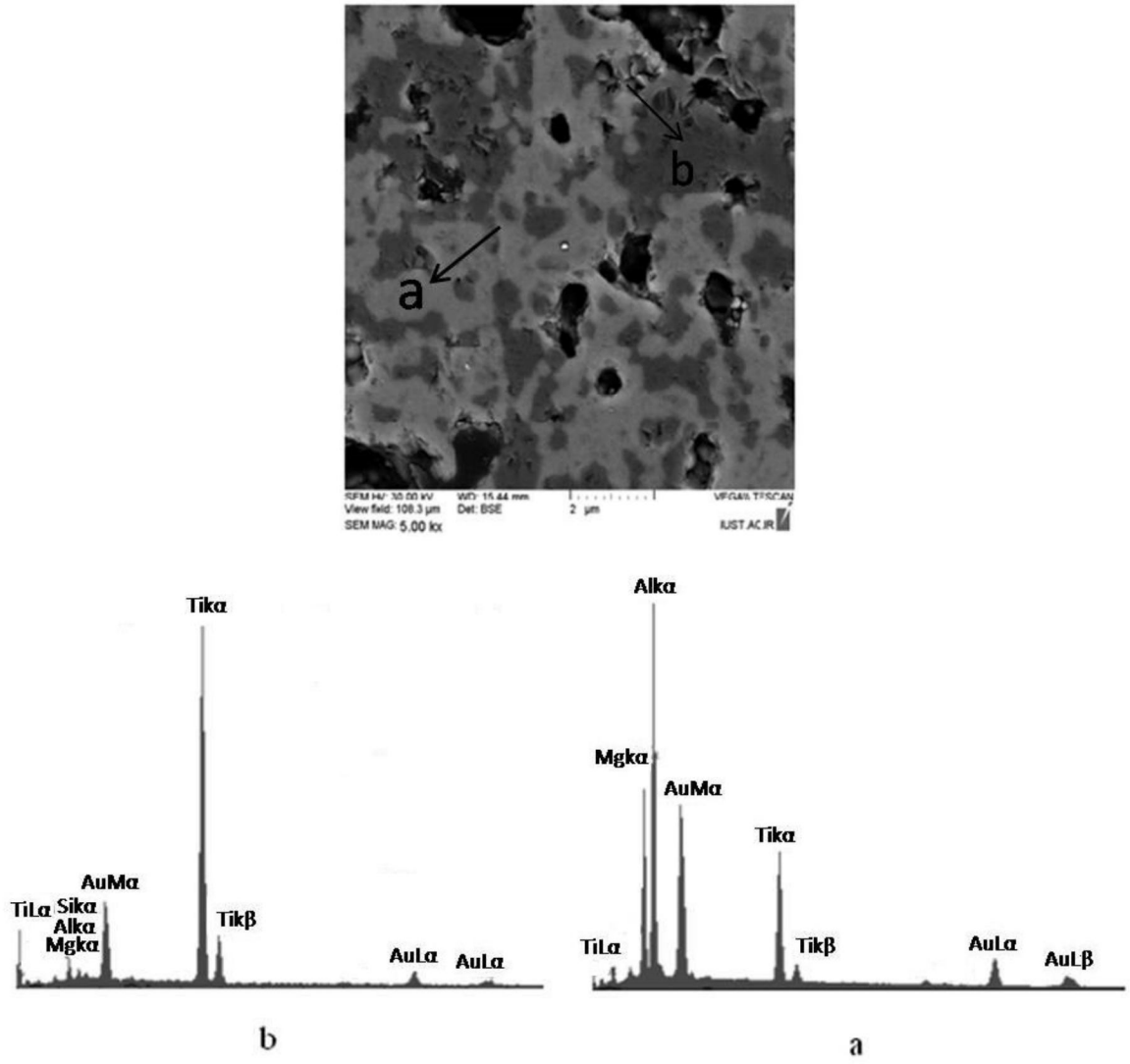

Fig. 5. Micrograph of sample that prepared by aluminothermic-carbothermal reduction at 1600°C a) EDX of bright phases b)EDX of dark gray phases.

accurately quantified by SEM-EDS.

Fig. 5 shows SEM micrograph of EB sample after firing at 1600˚C. As seen in this figure, the image composed of two phases: bright phases were surrounded by dark gray phases. According to EDS analysis of bright phases, this phase was rich of Ti and dark phase was rich of Mg and Al. SEM micrograph of EC sample is shown in Fig.6 and analysis of A and B points were done by EDS analysis. EDS analysis of B point in sample containing carbon black indicated that probably some Si ions as an impurity are present in these areas and caused to form more brighter area of Ti(C,N) phases.

SEM micrograph of ES sample which fired at 1400˚C is given in Fig. 7. As this image shows sample containing sugar has a very narrow fine particle size with uniform distribution.

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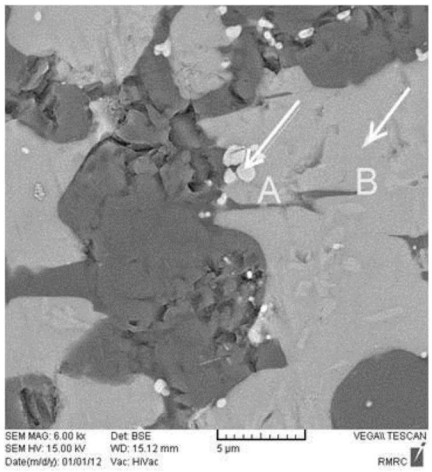

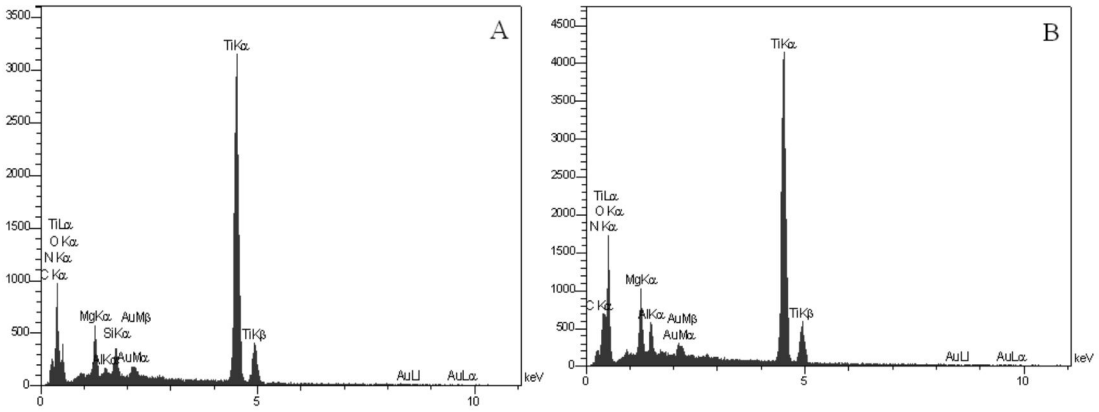

Fig. 6. Micrograph of EC sample after fired at 1600˚C A) EDX of A point B)EDX of B point

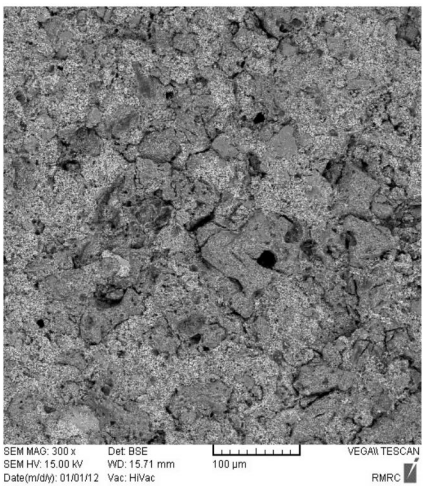

Fig. 7. Micrograph of ES sample after synthesized at 1400˚C

4. CONCLUSIONS

$MgAl_2O_4$-Ti(C,N) composites were synthesized without additive by aluminothermic reduction in coke bed condition at 1600˚C. Addition of carbon black and sugar in this composite were investigated. TiC and TiN peaks were observed at 1400˚C in sample containing carbon black by increasing temperature from 1400 to 1600˚C, the solubility of carbon inTi(C,N) solid solution increased significantly from 0.31 to 0.36. Addition of sugar to Al, MgO, TiO_2 mixture caused to decrease the synthesis temperature of $MgAl_2O_4$-Ti(C,N) composite from 1600˚C to 1400˚C and decrease the crystallite size of spinel and Ti(C,N) phase to 32 nm and 33 nm respectively and increase carbon

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content in $Ti(Cx,N_{1-x})$ to x=0.442 amount.

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