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Synthesis and comparison of $MgAl_2O_4$-Ti (C, N) composites using aluminothermic-carbothermal reduction and molten salts routes

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$MgAl_2O_4$-Ti (C, N) composites were synthesized through aluminothermic-carbothermal reduction and molten salts synthesis (MSS) routes in coke bed conditions. The phases were characterized using X-ray diffraction (XRD) and microstructures of composites were investigated by scanning electron microscopy (SEM). The results showed that the synthesis temperature of $MgAl_2O_4$-Ti (C, N) was decreased about 300 °C in MSS method in comparison with aluminothermic-carbothermal reduction. The KCl and NaCl salts proved better transportation path for reactant species and accelerate composite formation and also establish the microstructure with homogenous and fine grains.

Key words: $MgAl_2O_4$-Ti (C, N) composite ceramic, Coke bed, Molten salt.

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) has been recognized as an important refractory material in steel ladles and cement rotary kilns on account of its attractive properties such as high melting point (2135 °C), high chemical inertness, high thermal shock resistance, low thermal expansion coefficient [1, 2], and good resistance to alkaline slags [3]. Titanium carbonitride, Ti (C, N), has attracted due to its high melting temperature, high hardness, wear resistance, high electrical and thermal conductivities, good thermal and chemical stability [4, 5]. Comparison of the tensile properties and the modulus of Al-B_4C, Al-TiC, Al-SiC and Al-TiB_2 composites showed the advantages of Al-TiC. The Al-Ti-C system is also known to be of great interest in the grain refining industry [6].

$MgAl_2O_4$/Ti (C, N) composite ceramics may have good properties and potential application. $MgAl_2O_4$/TiN and $MgAl_2O_4$/Ti (C, N) composites have been synthesized in-situ from aluminothermic reduction and nitridation reaction [3]. But the reaction path in the molten salts has not been apparently reported up to now. This work deals the comparison of $MgAl_2O_4$-Ti (C, N) composites by the aluminothermic-carbothermal reduction and molten salts synthesis routes.

Experimental Procedures

Commercial aluminum powder (> 98%, d < 45 μm), TiO_2 (> 99%, anatase type, d_{50} = 3 μm), MgO powder (> 99%, periclase, d_{50} = 2 μm), nano size carbon black (Iran carbon Co), reactive alumina (Al_2O_3 > 99.8%, d < 2 μm), NaCl (> 99.5%) and KCl (> 99.5%) were used as starting materials.

The mixtures of Al, TiO_2, MgO were weighted according to the stoichiometry of reaction Eq.(1) with addition of 10wt.% carbon black to form $MgAl_2O_4$/Ti (C, N) in aluminothermic-carbothermal reduction. In molten salts route, Al_2O_3, MgO, TiO_2 and carbon black were weighted according to the stoichiometry of reaction in Eq.(2) to form anticipated products. The weight ratios of TiO_2 to carbon black to NaCl were 79.87 : 24.02 : 10.39 and also the weight ratios of Al_2O_3 to MgO to KCl were 71.8 : 28.2 : 30.0, respectively.

$$8Al + 6TiO_2 + 4MgO + 3N_2 = 4MgOAl_2O_3 + 6TiN \quad (1)$$

$$MgO + Al_2O_3 + TiO_2 + (3\text{-}x)C + X2N_2 = MgAl_2O_4 + Ti(C_x,N_{1-x}) + 2CO \quad (2)$$

The mixtures of raw materials with addition of 3 wt.% novalak resin as binder were prepared. Pellets of 10 mm in diameter were prepared by uniaxial pressing at 300 MPa. The dried pellets were buried in coke bed in bottom of crucible and heated in a furnace at 1100-1300 °C for salts contained samples and 1200-1600 °C for unsalts samples with 3 hrs soaking time with a rate of 10 °C/min. The X-ray diffraction patterns of samples were obtained using Philips X-ray diffractometer (Model PW3710) with CuKα radiation. The microstructures of samples were characterized by scanning electron microscopy (SEM, VEGAIIXMU).

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Results and Discussion

Phase evolution

Fig. 1 shows the X-ray diffraction (XRD) patterns of samples containing Al, TiO_2, MgO, carbon black and resin after firing at 1200-1600 °C in coke bed conditions. The aluminothermic-carbothermal reduction and nitridation can occur at this sample according to previously mentioned Eq. (1). According to this figure $MgAl_2O_4$ (MA) and $Mg_4Al_2Ti_9O_{25}$ (MAT) as main phases at 1200 °C and also small amount of TiO_2 (anatase and rutile) and Ti_nO_m were observed. Intensity of MAT peaks was decreased at 1400 °C, while TiC and TiN were appeared. At 1600 °C/3 hrs, the reaction completed and $MgAl_2O_4$/Ti(C, N) composite was established. The N_2 gas for nitridation of TiO_2 was provided from reaction of air with coke bed. The air contains 21 vol% oxygen and 79 vol% nitrogen. During firing under coke bed condition, the oxygen reacts with carbon and produce carbon monoxide. According to the reaction (3), the partial pressure of CO and N_2 would be about 3.5×10^4 and 6.5×10^4 Pa, respectively [5].

$$2C(s) + N_2(g) + O_2(g) = 2CO(g) + N_2(g) \quad (3)$$

MAT as an intermediate phase had pseudobrookite structure and is a solid solution of $MgTi_2O_5$ and Al_2TiO_5 which can be explained by the following reaction [7]:

$$Al_2O_3 + 9TiO_2 + 4MgO \rightarrow Mg_4Al_2Ti_9O_{25} \quad (4)$$

The increase of heat treatment temperature results in formation of Ti_nO_m which is a titanium oxide with lower degree of oxygen in comparison with TiO_2. Ti_nO_m, C and N_2 were reacted in reduction atmosphere and formed TiC and TiN. Ti (C, N) is solid solution of TiC and TiN, that dominated at 1600 °C.

Fig. 2 shows the XRD curves of samples containing Al_2O_3, TiO_2, MgO, carbon black, resin and salts, after firing at 1100-1300 °C in coke bed condition. During firing, salts start to melt and carbothermal nitridation occurred at presence of molten salts. As this figure shows $MgTi_2O_5$ and $MgAl_2O_4$ are main phases and rutile, TiN_xO_y, unreacted Al_2O_3 are minor phases at 1100 °C. Ti (C, N) phase was formed at 1200 °C and with increasing temperature up to 1300 °C spinel/Ti(C, N) composite was obtained. Formation of Ti (C, N) in samples containing salts and carbon black which related to carbothermal reduction reaction occurred with the following possible reaction series [5, 9].

$$aTiO_2(s) + bC(s) \rightarrow cTi_nO_m(s) + dCO(g) \quad (5)$$

$$aTiO_2(s) + bCO(g) \rightarrow cTi_nO_m(s) + dCO_2(g) \quad (6)$$

$$aTi_nO_m(s) + bN_2 \rightarrow cTiO_xN_y \quad (7)$$

$$aTiO_xN_y(s) + bC + CN_2 \rightarrow dTi(C,N) + eC(g) \quad (8)$$

$$aTiO_xN_y(s) + bCO_2 + cN_2 \rightarrow dTi(C,N) + eCO(g) \quad (9)$$

The occurrence of Ti_nO_m was resulted from TiO_2 reduction by carbon black and CO. The possible reason for the formation of TiO_xN_y was incorporation of nitrogen atoms into the Ti_nO_m, leading to the formation of solid solution, because Ti_nO_m such as Ti_3O_5 has a cubic crystal structure and nitrogen atoms have a strong tendency to be incorporated into this structure [5]. The presence of molten salts accelerates the diffusion of species and reduce formation temperature of Ti (C, N) from 1600 to 1300 °C in comparison with samples lacking from salts. The melting points of NaCl and KCl are known to be about 810 and 774 °C, respectively [5].

Formation of magnesium aluminate ($MgAl_2O_4$) spinel in molten salt occurs by template formation mechanism [9]. In this mechanism, one of the reactants is significantly more soluble than others. After dissolving of soluble reactant (MgO) in molten salts, their ions diffuse onto the surfaces of the less-soluble compound (Al_2O_3) and reacts in situ to form $MgAl_2O_4$. The dissolution temperature of MgO in molten chlorides clarifies the MA formation temperature; which for KCl and NaCl was 900 °C [5, 9]. Mg^+ ions have rapid diffusion into α-Al_2O_3 platelets in NaCl and KCl melts medium.

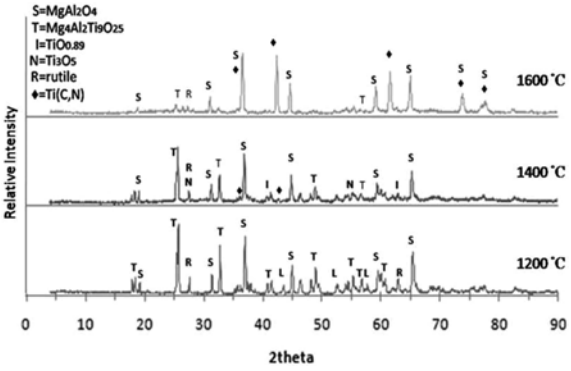

Fig. 1. XRD patterns of samples that prepared by alminothermic-carbothrmal reduction at different temperatures.

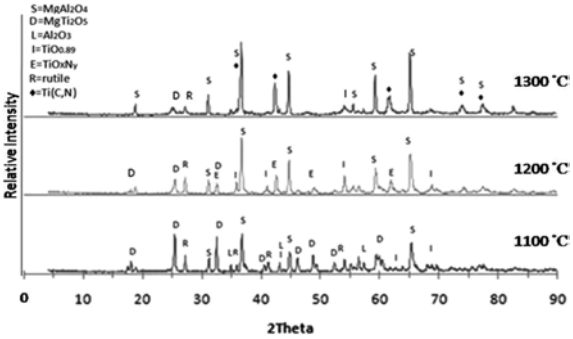

Fig. 2. XRD patterns of powder sample that prepared in present of molten salts.

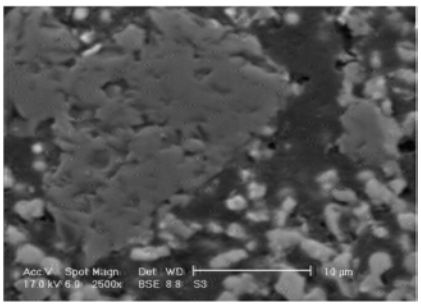

Fig. 3. SEM micrograph of sample that prepared by aluminothermic-carbothermal reduction at 1400 °C.

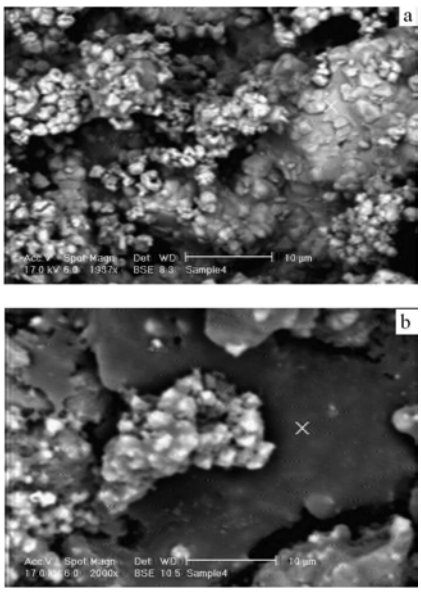

Fig. 4. SEM micrograph of samples that prepared by aluminothermic-carbothermal reduction at 1600 °C.

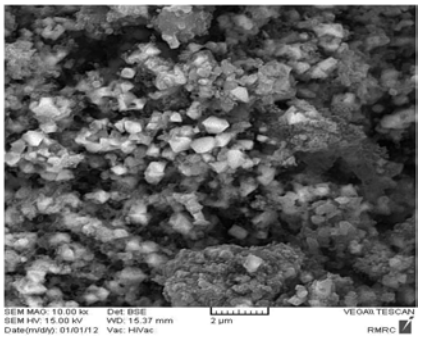

Fig. 5. SEM micrograph of prepared sample using NaCl and KCl at 1300 °C.

Microstructure analysis

SEM micrographs of samples that were prepared by aluminothermic-carbothermal reduction at 1400 and 1600 °C are shown in Figs. 3-4. Micrographs of sample synthesized at 1400 °C (Fig. 3) showed that different phases were obtained. The obtained crystalline phases (Fig. 1) were spinel, rutile, TiC, TiN and tialite. Fig. 4 shows SEM micrographs of synthesized sample at 1600 °C. According to this figure and XRD results (Fig. 1) spinel and Ti (C,N) phases were observed. Some spherical particles with 1-2 μm size observed and consolidated particle due to above temperature were also distinguished.

Fig. 5 shows SEM micrograph of the samples that were prepared using NaCl and KCl at 1300 °C. In the choosing method, the amounts of molten salts weren't enough to cause flow or deformation in samples. Also, the presence of carbon black caused to increase the refractoriness of samples. Therefore the size and morphology of the synthesized grains were two type, one similar to alumina and/or titania that obtained from molten salts route and other had new morphology that established from solid-state reaction sintering salts which were acted as a reaction medium that supplied a liquid phase medium at low temperature and aided to transportation of reactant species. Diffusion of different ions in molten salts medium is faster than the solid-state route, therefore the obtained composite have better uniformity (Fig. 4).

Conclusions

$MgAl_2O_4$-Ti (C, N) composites were synthesized through aluminothermic-carbothermal reduction and molten salts routes in coke bed conditions. Ideal yield of $MgAl_2O_4$-Ti (C, N) composites were obtained at 1600 °C by aluminothermic-carbothermal reduction and 1300 °C in presence of molten salts. The presence of NaCl and KCl had a strong positive effect on formation of Ti (C, N) during the reaction process which decreased reaction temperature and prompted significantly to the formation of Ti (C, N). In molten salts route the homogenous and fine microstructure ($d > 2$ μm) of $MgAl_2O_4$/Ti (C, N) composite formed at 1300 °C. The molten salts act better transportation medium of reactant species and accelerate reaction and formation of phases at relatively low temperatures.

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