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Fast synthesis of $MgAl_2O_4$–W and $MgAl_2O_4$–W–W_2B composite powders by self-propagating high-temperature synthesis reactions

J. Ghorbantabar Omran, M. Shafiee Afarani*, M. Sharifitabar

Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan P.O.Box: 98135-674, Iran

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ABSTRACT

$MgAl_2O_4$–W and $MgAl_2O_4$–W–W_2B composite powders were obtained rapidly in a single step by self-propagating high-temperature synthesis of WO_3–Mg–xAl_2O_3 and WO_3–B_2O_3–Mg–yAl_2O_3 systems. The addition of various Al_2O_3 contents (x and y-values) to the starting materials was considered as the main synthesis parameter. Thermodynamic calculations revealed that the adiabatic temperature of both systems was decreased with increasing Al_2O_3 content. The XRD results indicated that after acid leaching of the WO_3–Mg–xAl_2O_3 combustion products, W and $MgAl_2O_4$ were formed as the main phases and WO_2, $MgWO_4$ and Al_2O_3 as the minor constituents in the final composite. On the other hand, $MgAl_2O_4$–W composites were synthesized in the WO_3–B_2O_3–Mg–yAl_2O_3 system at $y < 1.4$ mol. By increasing the y-value to 2.1 mol, W_2B was formed as a new product leading to production of $MgAl_2O_4$–W–W_2B composite. The formation of spinel was confirmed by the Fourier transformed infrared spectroscopy analysis. Microstructure observations represented the uniform distribution of $MgAl_2O_4$ blocks within the fine spherical W particles. The melting of Al_2O_3 was found as a vital step for rapid synthesis of $MgAl_2O_3$ by the SHS route. Finally, the possible formation mechanism of $MgAl_2O_4$ during the combustion synthesis was proposed.

1. Introduction

Magnesium aluminate ($MgAl_2O_4$) spinel (MAS) has many applications in different ceramic industries owning to its unique properties. Those include high melting point (2135 °C), low density (3.58 g cm^{-3}), good resistance to chemical attacks, low thermal expansion between 30 and 1400 °C (9×10^{-6} $°C^{-1}$), resistance against thermal shock, high hardness and mechanical strength specially at elevated temperatures, optical properties, etc. [1–7]. Moreover, the strength and the toughness of the monolithic ceramics can be improved via the addition of secondary metallic or ceramic phases [8–10]. Therefore, $MgAl_2O_4$ containing composites have a potential for refractories and other application areas.

$MgAl_2O_3$ usually is synthesized by direct solid state reaction between MgO and Al_2O_3. However, the MAS has a lower density due to the large volume expansion (i.e. 5–7%) occurs during the formation of spinel [3]. This prevents the fabrication of a product with a desirable density after sintering process. To overcome this problem, the double firing process was proposed in which the raw materials were mixed and calcined at 1100–1350 °C for partial spinel formation (i.e. 55–70%). Then, the products were compacted after grinding and were sintered at 1700–1900 °C [3]. Due to the high production cost of the mentioned process, various alternative easy-echo routes were proposed such as; sol-gel [11,12], combustion synthesis [11,13–16], mechano-chemical synthesis [17,18], etc. Amongst these processes, combustion synthesis is a very simple, fast, cost effective and versatile route for the synthesis of different materials and composites [19–22]. During this process, the product is delivered aiding the heat liberated from an exothermic reaction. Depending on the ignition mode of the reaction, the combustion synthesis process is divided into two main categories as the volume combustion (VC) and the self-propagating high-temperature synthesis (SHS) routes [23].

So far, some efforts have been made to produce MAS and the composites containing this compound by the VC process. Peng et al. [16] showed that $MgAl_2O_4$ powders with the high spinel fraction and a narrow particle size distribution could be fabricated through infiltration of melted Al within the magnesia powders and its subsequent exothermic oxidation reaction in the air atmosphere. Li et al. [14] fabricated $MgAl_2O_4$–TiN composite through heating of the TiO_2–Al–MgO mixture at 1000 °C for 3 h in the N_2 atmosphere. Their results confirmed that the presence of MgO facilitated the production of TiN. In another experiment, synthesis of $MgAl_2O_4$–W composite was considered through the aluminothermic reduction of WO_3 in the presence of magnesia and excess alumina by Bingqiang et al. [13]. W was

* Corresponding author.
E-mail address: shafiee@eng.usb.ac.ir (M. Shafiee Afarani).

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incorporated into the ceramic matrix due to its high melting point, good thermal conductivity and its chemical inertness against the molten slag [13,24]. In this research, the WO_3–Al–MgO–xAl_2O_3 compacts were calcined at 1100 –1200 °C under coke protection for 3 h. The *x*-value varied between 0 and 2.1 mol to synthesize alumina rich MAS. They concluded that the MAS formed through a diffusion controlled solid state reaction between alumina and magnesia.

By reviewing the previous researches, it is observed that the aluminothermic VC process through heating of the raw materials at high temperatures for a long time were only performed for the combustion synthesis of MAS. However, to the best knowledge of the authors, there is no report on the fast synthesis of MAS and composites containing this compound via the SHS rout, especially through the magnesiothermic reactions of metal oxides in the presence of alumina.

The main goal of this research is the production of $MgAl_2O_4$–W and $MgAl_2O_4$–WB composite powders via the self-propagating high-temperature synthesis of the WO_3–Mg–xAl_2O_3 and WO_3–B_2O_3–Mg–yAl_2O_3 systems, respectively. The main advantages of the proposed process are rapid synthesis of composites containing MAS using inexpensive oxides as the starting materials, and also the elimination of the long heating times for the spinel formation.

2. Experimental procedure

WO_3 (Merck, 40–50 μm), B_2O_3 (Merck, 5–10 μm), Mg (Merck, < 200 μm) and high purity α-Al_2O_3 primary particles (WDR4, indal chemical, d50 = 1 μm, BET surface area 1.5 m^2/g and a purity of 99.4%) powders were used as the starting materials. The primary mixtures for the synthesis of $MgAl_2O_4$–W and $MgAl_2O_4$–WB composites were weighted based on the reactions 1 and 2, respectively.

$$WO_3 + 3Mg + xAl_2O_3 \rightarrow W + xMgAl_2O_4 + (3-x)MgO \quad 0.5 \leq x \leq 3 \qquad (1)$$

$$2WO_3 + B_2O_3 + 9Mg + yAl_2O_3 \rightarrow 2WB + yMgAl_2O_4 + (9-y)MgO \quad 0.7 \leq y \leq 2.1 \qquad (2)$$

The primary Al_2O_3 concentration was considered as the main process parameter to fabricate composites with various MAS contents. Different batches were mixed using a planetary mill with the ball/powder ratio of 10/1 for 10 min. Then, the resultant mixtures were uniaxially pressed into a cylindrical steel die to prepare green compacts with 12 mm diameter, 13–21 mm height and 58–60% theoretical density. The SHS reaction was ignited from the top surface of the compacts in a closed chamber containing Ar gas. The details of the chamber and the ignition process have been reported elsewhere [25]. The unwanted phases were purified by acid leaching using 37 vol% HCl solution at 100 °C for 5 h under magnetic stirring. Finally, the obtained powders were washed with distilled water and dried at 100 °C in an electric oven.

Structural analysis of the samples was performed using X-ray diffraction (XRD, Bruker Advanced D8) technique with the Cu Kα radiation. Molecular analysis was performed by a Fourier transform infrared spectroscopy (FTIR, Bruker TENSOR II) in the range of 400–4000 cm^{-1}. The microstructure of the products was studied by scanning electron microscope (SEM, KYKY EM3900M) and field emission scanning electron microscope (FESEM, MIRA3 TESCAN) equipped with energy dispersive spectroscopy (EDS, SMAX).

3. Results and discussion

3.1. Thermodynamic considerations

In the exothermic reactions, the liberated heat can increase the temperature of the products. If it is assumed that there is no heat loss to the surrounding medium (i.e. the system conditions assumed to be adiabatic), the highest theoretical temperature that products could

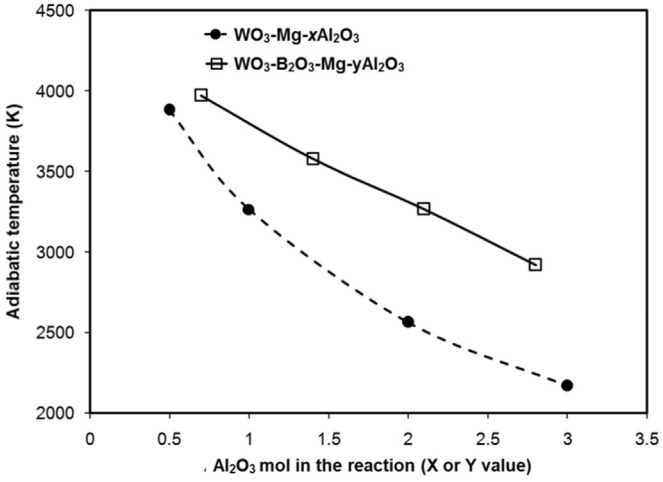

Fig. 1. Adiabatic temperature of the WO_3–Mg–xAl_2O_3 and WO_3–B_2O_3–Mg–yAl_2O_3 systems versus primary Al_2O_3 contents.

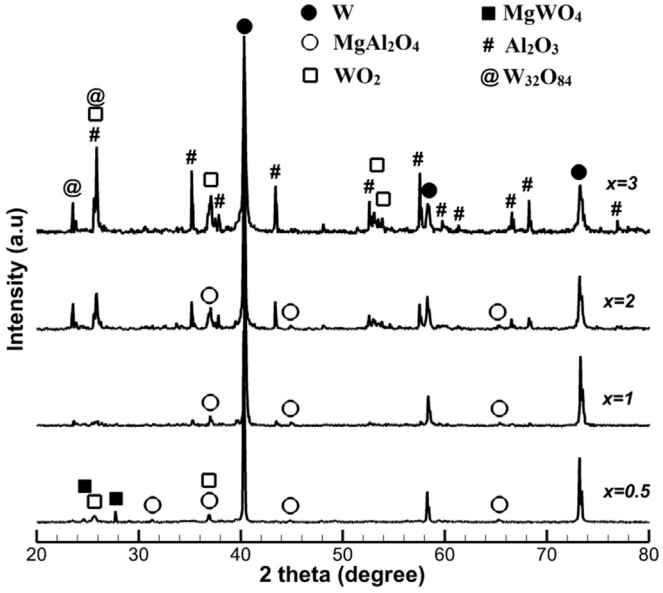

Fig. 2. XRD patterns of the combustion products in the WO_3–Mg–xAl_2O_3 system containing different Al_2O_3 contents.

experience (T_{ad}) can be calculated by the following equation [23,25]:

$$-\Delta H^0_{298} = \int_{298}^{T_{tr}} nC_p(products)dT + n\Delta H_{tr} + \int_{T_{tr}}^{T_{ad}} nC_p(products)dT \qquad (3)$$

where ΔH^0_{298} is the formation molar enthalpy difference between the products and the raw materials at 298 K, *n* denotes to the mole of each product and C_p is its heat capacity. The phase change in each product at a specified temperature (T_{tr}) along with its corresponding molar enthalpy of transformation (ΔH_{tr}) also should be considered in the calculations. Moreover, a diluents agent is assumed as a product. Usually, the lower adiabatic temperature will result to the slower combustion front velocity [23]. Based on the experimental Merzhanov criterion [19], the combustion reaction can be proceed in the self-sustaining mode if $T_{ad} \geq 1800K$. In this condition, the process is called self-propagating high-temperature synthesis (SHS). Fig. 1 shows the effect of Al_2O_3 additions to the initial reactants on the adiabatic temperature of WO_3–Mg–xAl_2O_3 and WO_3–B_2O_3–Mg–yAl_2O_3 systems. As illustrated, the adiabatic temperature of the latter system was generally higher than the former system for the same Al_2O_3 contents. Moreover, the adiabatic temperature of the both systems decreased with increasing Al_2O_3