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OXIDATION OF THE Al_2O_3-TiB_2 COMPOSITES PRODUCED WITH THE REDUCTION-COMBUSTION SYNTHESIS TECHNIQUE

OKSIDACIJA KOMPOZITA Al_2O_3-TiB_2, IZDELANEGA S TEHNIKO REDUKCIJSKE ZGOREVNE SINTEZE

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In this study, Al_2O_3-TiB_2 composites were synthesized in an electrical resistance furnace in open atmosphere under the uniaxial pressure of 150 MPa at 1200 °C for 4 h, using the reduction-combustion synthesis technique. The initial powder mixture used in this study is $Al+TiO_2+B_2O_3$. TiB_2, Al_2O_3 and some trace phases were found in the produced composites using the X-ray diffraction analysis. The densities of the samples were measured using the Archimedes' technique. The relative density was determined as 94.2 % for the composites. The oxidation properties of the composites were examined in open atmosphere at 600 °C, 800 °C and 1000 °C after up to 64 h. The activation energy of the composite was calculated to be 90 kJ/mol.

Keywords: composite, sintering, reduction combustion synthesis, oxidation

V tej študiji je bil sintetiziran kompozit Al_2O_3-TiB_2 v električni uporovni peči z normalno atmosfero pri enoosnem tlaku 150 MPa in 4 h pri 1200 °C z uporabo tehnike redukcijske zgorevne sinteze. Začetna mešanica prahov, uporabljena v tej študiji, je bila $Al+TiO_2+B_2O_3$. Z rentgensko difrakcijo so bili v izdelanem kompozitu odkriti TiB_2, Al_2O_3 in nekaj faz v sledovih. Gostota vzorcev je bila izmerjena z Arhimedovo tehniko. Relativna gostota kompozita je bila 94,2-odstotna. Oksidacijske lastnosti kompozita so bile preiskane na zraku po 64 h na temperaturah 600 °C, 800 °C in 1000 °C. Izračunana aktivacijska energija kompozita je bila 90 kJ/mol.

Ključne besede: kompozit, sintranje, redukcijska zgorevna sinteza, oksidacija

1 INTRODUCTION

Reduction (thermite type) combustion synthesis (RCS) is one of the three main types of combustion synthesis from the viewpoint of chemical nature.[1] The in-situ synthesis is used for fabricating the metal- or ceramic-matrix composites.[2] As the reinforcements are generated directly from the chemical reaction within the matrix, the composites show many excellent advantages, such as a clean reinforcement-matrix interface, fine and thermodynamically stable reinforcement, good compatibility and high bonding strength between the reinforcement and the matrix, and low fabrication costs.[3] When TiC or TiB_2 are combined with Al_2O_3, the composite, without a significant drop in the hardness, has a better oxidation resistance and possesses a superior mechanical strength and fracture toughness than TiC or TiB_2 alone. Researchers have chosen reduction (thermite type) combustion synthesis systems like TiO_2/Ti-B_2O_3/B-Al, Nb-B-Al-Nb_2O_5, ZrO_2-B_2O_3-Al, TiO_2-Al for fabricating the Al_2O_3 based in-situ composites.[4–6] The main objective of the present study is to investigate the synthesis of the Al_2O_3-TiB_2 in-situ composites produced from TiO_2, B_2O_3 and Al precursors with the one-step, pressure-assisted, reduction-combustion technique, and the oxidation properties of the produced composites.

2 EXPERIMENTAL DETAILS

The Al_2O_3-TiB_2 in-situ composite was densified by uniaxial loading during the reaction. TiO_2 (98.8 % purity, 1 µm), B_2O_3 (99.99 % purity, less than 38 µm) and Al (99 % purity, 15 µm) were used in the powder mixtures to produce the TiB_2-Al_2O_3 composites using the aluminothermic reduction. The mixed powders were pressed in a cylindrical mold, then the in-situ composite was formed in an electrical resistance furnace in open atmosphere under a uniaxial pressure of 150 MPa, at 1200 °C, with a heating rate of 20 °C/min and for 4 h. To examine the relative density, the Archimedes' method with a sensitive balance (0.0001 g) was applied. The specimens were polished with the emery papers (up to 1200 grit) and, finally, with a diamond paste up to 1 µm before the oxidation test. The oxidation properties of the samples were investigated at 600 °C, 800 °C and 1000 °C for (4, 16, 32 and 64) h in open atmosphere. Each sample was carefully weighed before and after the oxidation test to determine the weight changes. The morphology and nature of the oxide layer and the phases formed in the oxidized layers of the samples, tested at 600 °C, 800 °C and 1000 °C for 64 h, were characterized using the SEM and XRD analyses. In order to understand the kinetics of the oxidation, the data were analyzed using the parabolic law:

$$\left(\frac{\Delta w}{A}\right)^2 = k_\mathrm{p} t \tag{1}$$

where Δw is the change in the weigh, A is the surface area of the sample, t is the oxidation time and k_p is the parabolic rate constant.[7]

3 RESULTS AND DISCUSSION

The composite produced with the pressure-assisted RCS is compact and dense. This technique is more advantageous than the classic two-step production methods. The aluminothermic reaction results in the Al_2O_3-TiB_2 composite according to the following reaction:

$$3TiO_2+3B_2O_3+10Al \rightarrow 5Al_2O_3+3TiB_2 \tag{2}$$

TiB, TiO_2 and the Al_5BO_9 trace phases, along with the major Al_2O_3 and TiB_2 peaks, were observed during the XRD analysis (**Figure 1**). The Al_2O_3-TiB_2 composite with the calculated volume proportions of Al_2O_3 (71 %) and TiB_2 (27 %) was obtained with a synthesizing system of $3TiO_2$-$3B_2O_3$-10Al.[8] In the present study, the relative densities of the samples, synthesized under a pressure of 150 MPa and at 1200 °C for 4 h, were measured as 94.2 %.

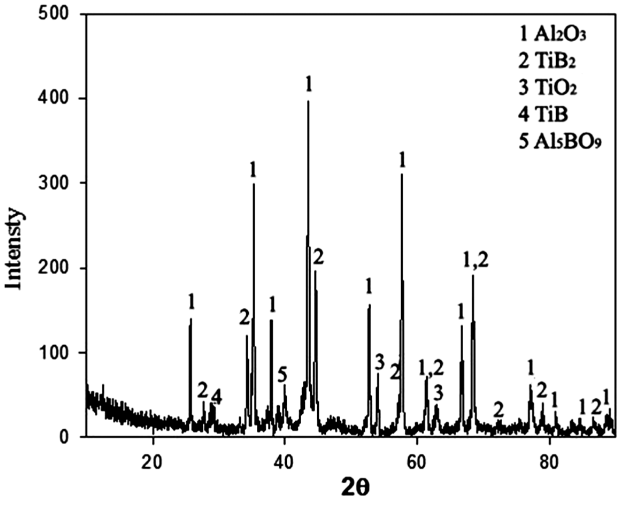

Figure 1: XRD diffraction patterns of the synthesizing at 1200 °C for 4 h

Slika 1: Rentgenska difrakcija sintetiziranega kompozita po 4 h na 1200 °C

Table 1: Variation in the weight gain as a function of the process time and temperature

Tabela 1: Spreminjanje prirastka mase v odvisnosti od časa in temperature procesa

Time (h)	Weight change (g/cm^2)		
	600 °C	800 °C	1000 °C
4	0.587	1.493	2.322
16	0.618	2.899	3.277
32	0.709	3.123	3.738
64	0.782	3.322	4.371

The mass change of the oxidized samples during the oxidation treatment at 600 °C, 800 °C and 1000 °C as a function of the process time for the Al_2O_3-TiB_2 composites occurred parabolically with the process time. The mass changes of the composites during the oxidation test at 600 °C, 800 °C and 1000 °C, lasting for 4–64 h, are listed in **Table 1**.

The parabolic rate constant was calculated from the slope of the plots that was drawn from the square of the mass change versus the treatment time of the composites. The parabolic rate constants (k_p) of the composites during the oxidation tests at 600 °C, 800 °C and 1000 °C are $0.322\cdot10^{-5}$ g^2/(cm^4 s), $5.98\cdot10^{-5}$ g^2/(cm^4 s), and $9.59\cdot10^{-5}$ g^2/(cm^4 s), respectively. The temperature dependence of the parabolic rate constant (k_p) follows an Arrhenius-type expression, $k_\mathrm{p} = k_\mathrm{o} \exp(-Q/RT)$. The slope of the plots that was drawn from the $L_\mathrm{n}K_\mathrm{p}$-values versus $1/T$ is to give the Q/R-value. In the present study, the calculated value of the activation energy was approximately 90 kJ/mol in the temperature range of 600–1000 °C, for the Al_2O_3-TiB_2 composite.

Tampieri and Bellosi[9] have reported the activation energy of 230 kJ/mol (T = 400–900 °C) and 40 kJ/mol (T = 900–1100 °C) for the monolithic TiB_2. An activation energy of 110.56 kJ/mol was reported for the temperature range of 750–950 °C by Murthy et al.[10] Murthy et al. explained that the vast difference in the activation energy for the TiB_2 oxidation with the temperature is due to the change in the mechanism caused by the evaporation of B_2O_3 at higher temperatures. The SEM images of the oxidized surfaces of the composites at 1000 °C for 64 h are shown in **Figure 2**. The cracks, along with the coarsening of the oxide, were observed on the surface of the sample oxidized at 1000 °C. The results presented are consistent with the study of Murthy et al.[7] A large volume expansion was seen during the oxidation of the composites. During the oxidation process, the TiB_2 phase oxidized and, subsequently, changed to the TiO_2 phase. During the oxidation, the transformation of the TiB_2 phase to TiO_2 causes a cracking of the oxide layer, resulting in an increase in the active area for further oxidation.[7] Because of the active area formed by the cracks, the oxide layer was thought to accelerate this mechanism. The oxide layer was charac-

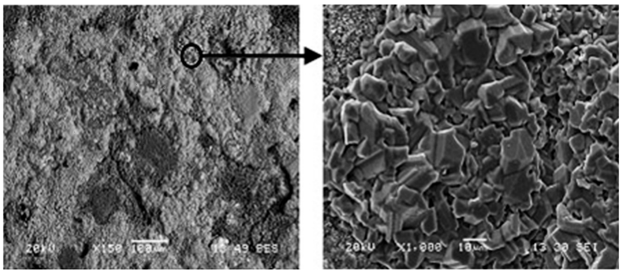

Figure 2: SEMs of the oxidized surfaces of the composites at 1000 °C after 64 h

Slika 2: SEM-posnetka oksidirane površine kompozita po 64 h na 1000 °C

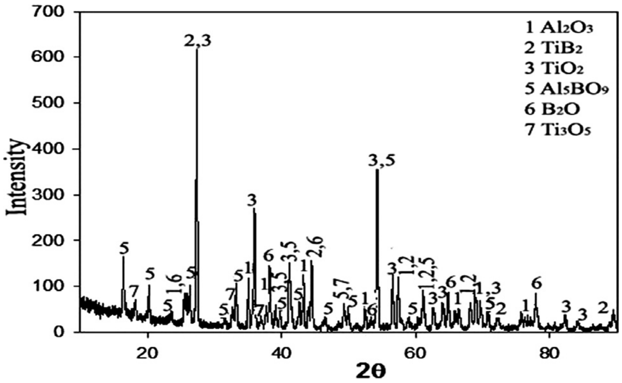

Figure 3: XRD patterns of the oxidized surfaces of the composite specimens at 1000 °C after 64 h

Slika 3: Rentgenska difrakcija oksidirane površine vzorca po 64 h na 1000 °C

terized by the presence of the surface cracks, probably caused by either the large volume expansion of B_2O_3 or the thermal stresses generated during the cooling.[11] The X-ray diffraction patterns of the oxidized undoped and doped composites at 1000 °C for 64 h are given in **Figure 3**.

The phases formed in the oxidized layer of the composite materials at 1000 °C after 64 h were the TiO_2, B_2O, Al_5BO_9 and Ti_3O_5 phases, besides the Al_2O_3 and TiB_2 phases. Possible reactions of TiB_2, B_2O_3 and Al_2O_3 are:

$$TiB_2+5/2O_2 \rightarrow TiO_2+B_2O_3$$
(solid if $T < 450$ °C, and liquid if $T > 450$ °C), (3)

$$5/2Al_2O_3+1/2B_2O_3 \rightarrow Al_5BO_9 \qquad (4)$$

TiO_2 is a semi-protective oxide formed at a high temperature. Depending on the defect concentration, the growth of TiO_2 is governed by either an outward diffusion of the interstitial Ti ions or an inward diffusion of the oxygen ions via the vacancies.[11] It is possible that B_2O_3 has the dominant effect on the oxidation of the TiO_2 phase.

4 CONCLUSION

This study reports on the oxidation properties of an Al_2O_3-TiB_2 in-situ composite obtained with the pressure-assisted, reduction-combustion synthesis of the thermite mixtures. The mass (the weight gain) of the oxidized samples during the oxidation treatment in open atmosphere at 600 °C, 800 °C and 1000 °C as a function of the process time (up to 64 h) for the Al_2O_3-TiB_2 composites was changing parabolically with the process time. The activation energy of the composites was calculated to be 90 kJ/mol.

Acknowledgement

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