Oxidation behavior of AlMgB₁₄-TiB₂ composite at elevated temperature

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Abstract: The isothermal oxidation behavior of AlMgB₁₄-TiB₂ composite was investigated at the temperature range from 600 °C to 1000 °C in air for 10 hours. The results showed that the oxidation kinetics of this composite obeyed the parabolic law with an activation energy of $176 \pm 20 \text{ KJ} \cdot \text{mol}^{-1}$ from 700 °C to 1000 °C, the corresponding parabolic rate constant increased from $0.0069 \times 10^{-8} \text{ kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ to $138.75 \times 10^{-8} \text{ kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$. The SEM micrograph of the oxidized surface at 700 °C for 10 h indicated that only the TiB₂ phase was changed. The AlMgB₁₄ phase changed at 800 °C in air, and the oxide scale consisting of TiO₂ and borate glass dissolved with MgO and Al₂O₃. Meanwhile, a number of pores also existed in the oxide scales. The oxide scales at 1000 °C were divided into three layers: an outer glassy B₂O₃ layer, a middle oxide layer with small size pores, and a reaction layer with large size pores formed as the oxidation of the AlMgB₁₄ phase. The formation mechanism of the oxidized layers was analyzed.

Keywords: AlMgB₁₄-TiB₂ composite; Isothermal oxidation; Layer; Mechanism

1 Introduction

B-rich compounds that consist of B₁₂ icosahedra have intrigued numerous investigations owing to their interesting properties and potential technical applications in the field of nuclear energy, aerospace and military hardware [1]. Recently, researchers discovered a B₁₂-based ternary compound AlMgB₁₄, which has been given great attentions for its excellent properties such as super-hardness, low density, and good electrical conductivity [2-5]. It was reported that the Vickers

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hardness of AlMgB_{14} are 27.4-28.3 GPa [6], 32-35 GPa [2], and 40 GPa [7] for single crystal, polycrystal and amorphous films, respectively. A. Ahmed et al. [8] investigated that with the addition of 60-70 wt.% TiB_2 , the hardness increased from 28.2 GPa in the single phase to 36.8 GPa in the composite, and the fracture toughness was seen to increase from 2.97 to 4.07 $\text{MPa}\cdot\text{m}^{1/2}$. With its high hardness and relatively low cost, AlMgB_{14} matrix composite is a promising super-hard material for replacing expensive c-BN and diamond, and it can also be used in cutting, grinding, polishing operations, and wear-resistant coating.

As a new engineering ceramic, the environmental stability is an important criterion for its actual applications, since the material will be inevitably exposed to high temperatures. There have been several reports [9-12] on the synthesis and mechanical performance of $\text{AlMgB}_{14}\text{-TiB}_2$ ceramic. However, the oxidation behavior of $\text{AlMgB}_{14}\text{-TiB}_2$ was not available in the open literature. In the present study, AlMgB_{14} matrix composite with 30 wt.% TiB_2 as the strengthening and binding phase were synthesized by using the FAPAS method [9, 13-15]. The isothermal oxidation behavior of $\text{AlMgB}_{14}/\text{TiB}_2$ composite from 600 °C to 1000 °C in air for 10 h was investigated.

2 Experimental

2.1 Preparation of $\text{AlMgB}_{14}\text{-TiB}_2$ ceramics

$\text{AlMgB}_{14}\text{-TiB}_2$ composite with $\text{AlMgB}_{14} : \text{TiB}_2$ molar ratios of 7:3 (denoted as AT73) was prepared by the FAPAS method [9, 15], in which AlMgB_{14} , and TiB_2 powders protected by a high pure argon atmosphere were pressed in a graphite die at 1400 °C for 10 min under an applied pressure of 60 MPa. The generated current was 1400A DC and the ultimate vacuum was 6.67×10^{-3} Pa. The AlMgB_{14} powders were obtained by mechanically milling a mixture of individual elements of Al, Mg and B

powders in an atomic ratio of 1: 1: 14 using a planetary high-energy ball-mill under high-purity argon atmosphere. Density of samples was measured using the Archimedes method. The Vickers hardness was determined by an HV-1000 type micro-hardness tester, using a load of 1 kgf and a dwell time of 10 s. Each hardness value reported was the average value of 15 repeated measurements. The fracture toughness was calculated using the formula of Anstis et al [16].

Fig. 1

2.2 Oxidation and characterization

The isothermal oxidation test was carried out from 600 °C to 1000 °C for 10 h. Specimens with a dimension of 10×3×4 mm³ were cut out from the sintered bodies and machined with a 600-grit diamond wheel and subsequently polished with the diamond polishing paste down to 1µm. Subsequently, the specimens were ultrasonically cleaned in acetone and ethanol, and then suspended using Pt wires in an air-atmosphere tube furnace equipped with a thermobalance, the accuracy of thermobalance was ± 0.1 mg. The oxidation kinetics was measured by monitoring the relation between the weight change and the oxidation time. The phases of the oxidation layer under high temperature were examined by using a computer-controlled diffractometer with Cu Kα radiations (XRD-6100, SHIMADZU, Japan). The microstructure of both the oxidation surface and the cross-section of the oxidized samples were characterized by an SEM (S-3400, HITACHI, Japan) and its EDS attachment.

3 Results and discussion

3.1 Microstructure and mechanical properties

The typical microstructure of AlMgB₁₄-30 wt.%TiB₂ composite is presented in Fig.1a. The SEM image reveals that the super-fine TiB₂ grains (gray) are diffusely distributed in the AlMgB₁₄ matrix phase (black). A few MgAl₂O₄ (bright white) were also detected on the surface of the precursor powers, which was contaminated by the oxygen in the process of the sample preparation. Fig. 1b

illustrates that AlMgB_{14} , TiB_2 , and MgAl_2O_4 are identified as the crystalline phases in the as-synthesized composite. The diffraction peak of TiB_2 is dominant, which is related to a high electron density of TiB_2 . AT73 exhibits the highest average hardness value of 31.5 GPa with an actual density of $3.15 \text{ g}\cdot\text{cm}^{-3}$ and a lowest relative density of 97.6 %. The porosity amounts of the sample is 2.38 %, meanwhile, fracture toughness changes from 3.0 to $3.95 \text{ MPa}\cdot\text{m}^{1/2}$ after adding 30 wt.% TiB_2 particles.

3.2 Oxidation kinetics

The mass variations of AT73 at different oxidation temperatures changes with the oxidation time are plotted in Fig. 2a. It is seen that the weights of samples show almost no change after being oxidized at 600 °C for 10 h, and the oxidation behaviors of AT73 were investigated only at 700 °C and above. Even after oxidation at 800-900 °C for 10 h, the weight change was less than 1.5 %. When the oxidation temperature is as high as 1000 °C, the sample has a relatively high mass change of 6.75 % after oxidation for 10 h.

Fig. 2

The parabolic rate law was used in order to determine the oxidation kinetics of AT73 ceramic. The plots of weight gain per unit area versus the square root of oxidation time are depicted in Fig. 2b. The linear curves indicate that the oxidation kinetics of AT73 was in agreement with the parabolic rate law in the oxidation temperature range of 700-1000 °C. According to the parabolic rate law, the square of the weight gain per unit area changes with the oxidation time was expressed as follows:

$$\Delta m^2 = k_p * t \quad (3.1)$$

Where Δm (mg/cm^2), t (h), and k_p ($\text{kg}^2\cdot\text{m}^{-4}\cdot\text{s}^{-1}$) are the mass gain, the oxidation time, and the parabolic rate constant, respectively. The values of k_p , slope of the plots in Fig. 2b, were listed in

Table 1. It can be seen that the parabolic rate constant k_p increases from $0.0069 \times 10^{-8} \text{ kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 700 °C to $138.75 \times 10^{-8} \text{ kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 1000 °C. The plot of $\ln k_p$ versus $1/T$ was shown in Fig. 3 and was fitted to a line. The apparent activation energy can be determined from an Arrhenius-type equation [17] (3.2). E_a in the equation means the effective activation energy for oxidation, and illustrates the ease of oxidation process. The parabolic law assumes that the oxidation rate is diffusion controlled. The activation energy was calculated to be $176 \pm 20 \text{ kJ} \cdot \text{mol}^{-1}$ in the oxidation process of 700-1000 °C.

$$k_p = A \exp\left(\frac{-E_a}{RT}\right) \quad (3.2)$$

Where A, R, T are a constant, the universal gas constant, the absolute temperature, respectively.

Fig. 3

Table 1

3.3 X-ray diffraction phase analysis

In order to understand the oxidation process of AT73, X-ray diffraction patterns of the surface layer of the oxidized AT73 at the temperatures range of 600-1000 °C for 10h are shown in Fig .4. It can be seen that no new phase was detected for the specimens oxidized at 600 °C comparing to the XRD pattern at room temperature. When the samples were oxidized between 700 °C and 900 °C, TiO_2 was newly identified from the XRD pattern, meaning the TiB_2 phase was oxidized. When the oxidation temperature raised up to 800 °C and 900 °C for 10 h, in addition to the detected phase, the newly appeared diffraction peaks indicate that the probable presence of $\text{MgO}(\text{B}_2\text{O}_3)_2$ (magnesium borate) and $(\text{Al}_2\text{O}_3)_{10}(\text{B}_2\text{O}_3)_2$ (aluminum boron) in the oxide layer, which indicates that the oxidation of AlMgB_{14} phase occurs when AT73 was oxidized at 800 °C in the air. When the

oxidation temperature was 1000 °C, only B₂O₃ and TiB₂ diffraction peaks were detected.

Fig. 4

3.4 Analysis of the surface and the cross-section of the oxidized AT73

3.4.1 Surface morphologies

The SEM micrographs of the specimens after oxidation at various temperatures for 10 h are shown in Fig. 5. Table 2 gives the results of the EDS analysis in the marked points. The presence of carbon was due to the contamination of the detector in the SEM observation, and the trace of calcium was introduced as an impurity element.

Fig. 5

Table 2

When the specimen was exposed to air at the temperature of 700 °C for 10 h, only the morphology of TiB₂ changed noticeably. Meanwhile, there are many pores formed on the oxidized surface because the interfaces of different phases were destroyed. The EDS analysis in point (2) shows that the white phase was TiO₂ as a result of the oxidation of TiB₂. When the temperature was increased to 800 °C, a continuous black oxide phase appeared with small acicular precipitates from the oxidized surface. Meanwhile, several small pores were found. The EDS in point (3) shows that boron element content is much less than at point (1), indicating that the black AlMgB₁₄ phase was oxidized at 800 °C. When the oxidation temperature was increased to 900 °C, a large amount of acicular and granular oxide precipitated from the glassy area, and some blocky dark phases were formed as well. The EDS in point (5) shows that the glassy area contained substantial amounts of O and B elements. Combining with the result of XRD analysis, it can be concluded that these areas were of partial borate glass. The EDS in Point (6) indicates that the blocky dark phase probably was Magnesium Borate glass. Point (7) shows that the glassy layer with some stomas was composed of B₂O₃.

3.4.2 SEM micrographs of cross-sections of the oxidized AT73

Fig. 6 shows that the thickness of the oxidized layer significantly changed at the oxidation temperature above 700 °C, from about 4.1 μm at 700 °C to about 84 μm at 1000 °C after it was oxidized for 10 h. Fig. 7a gives the typical cross-sectional morphology of the oxidized layer after 1000 °C for 10 h. It can be seen that the oxidation layer consists of three obvious separated parts, and the corresponding results of both line scanning and point scanning analysis show that the area I in the outer layer is borate glass, and the area II which is the intermediate layer contains some small size pores, and primarily of aluminum oxide, magnesium oxide, titanium oxide. Area III contains large pores and the EDS analyses in this region (see Fig. 7b) indicates that the main phase in the area III contained substantial amounts of Ti and B elements. Oxygen could not be detected by EDS so that only the MgAlB₁₄ phase oxidized in the area III whereas the TiB₂ phase was not oxidized. Area IV is unoxidized material.

Fig. 6

Fig. 7

3.5 Transport in the oxidation process

The surface of the samples began to oxidize at 700 °C, and the TiO₂ phase and large size pores were formed as the result of the oxidation of TiB₂. The following reaction may occur [18, 19, 20, 21]

At a higher oxidation temperature (≥ 800 °C), the matrix AlMgB₁₄ phase also started to be oxidized. In addition, TiO₂, Al₂O₃, MgO, the liquid glassy B₂O₃ were generated and formed a protective scale with Al, Mg and B atoms diffused outward to the surface. As a result, the weight

gain rate of AT73 was less than 1.5% when it was oxidized at 900 °C for 10 h. As B₂O₃ is acid oxide, it could dissolve a part of Al₂O₃ and MgO, and transfer into (Al₂O₃)₁₀(B₂O₃)₂ (aluminum boron) and MgO(B₂O₃)₂ (magnesium borate).

The overall reaction of the oxidation of AlMgB₁₄ phase probably was:

However, with a further increase in temperature to 1000 °C, a protective oxide layer formed at the initial stage of the oxidation of AT73, the phase composition of this oxidation layer was composed of TiO₂, aluminum boron and magnesium borate glass. While O diffuses inward to the matrix through pores distributed in the oxide layer, the oxygen partial pressure changes. The oxygen pressure in the reaction layer is much lower than that in the outer environment. Low oxygen pressure favors the oxidation of MgAlB₁₄ rather than TiB₂ phase, As a result of the oxidation of MgAlB₁₄, a large amount of B₂O₃(l) overflowed by passing the pores from the reaction layer and formed a B₂O₃ glassy layer (seen in area I), and also left numerous large size pores in the area III. Meanwhile, a large number of oxides were generated and gathered in the area II .

4 Conclusions

(1) The oxidation resistance of AlMgB₁₄-TiB₂ composite is investigated at 600-1000 °C for 10h in air. The oxidation kinetics of AT73 is in agreement with the parabolic law with an activation energy of $176 \pm 20 \text{ KJ} \cdot \text{mol}^{-1}$ from 700 °C to 1000 °C. The weight change of AT73 is less than 1.5% when oxidized at 900 °C for 10 h, while the figure increases to 6.5% after being oxidized at 1000 °C for 10 h.

(2) When the oxidation temperature is 700 °C, only the TiO₂ phase is formed due to the oxidation of TiB₂ and also several pores are left. When the oxidation temperature is 800 °C and above, the matrix phase of AlMgB₁₄ also changes, and the oxidized surface is composed of TiO₂, MgO, Al₂O₃,

and glassy B_2O_3 . The thickness of the oxidized layer is less than 10 μm .

(3) The cross-section of the oxide scale is divided into three layers after oxidized at 1000 °C for 10 h: the outer glassy B_2O_3 layer, the middle layer contained mixed oxides and small pores, and the underlying reaction layer contained large pores and TiB_2 phase which has not been oxidized.

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Ethical standards

The work has been performed in accordance with the ethical standards laid down in the 1964 Declaration of Helsinki. All the authors agree to submit the paper to <Applied Surface Science>.

Conflict of interest

This study was supported by National Science Foundation of China and Shanxi Province Science Foundation for Youth. The authors declare that they have no conflict of interest.

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Fig. 1

Fig. 2a

Fig. 2b

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7a

Fig. 7b

Table caption

Table 1 The oxidation rate constants of AT73 oxidized at different temperatures for 10h

Table 2 Average chemical composition of label area in Fig. 5 measured by EDS

Table 1 The oxidation rate constants of AT73 oxidized at different temperatures for 10h

Temperature/°C	Parabolic rate constants $k_p/\text{kg}^2\cdot\text{m}^{-4}\cdot\text{s}^{-1}$
700	0.0069×10^{-8}
800	0.83×10^{-8}
900	3.36×10^{-8}
1000	138.75×10^{-8}

Table 2 Average chemical composition of label area in Fig. 5 measured by EDS

Point	Element (wt.%)							Major corresponding phase
	Al	Mg	B	O	C	Ca	Ti	
1	3.67	5.13	53.90	6.51	28.11	0.38	2.30	AlMgB ₁₄
2	0.74	0.93	0	45.87	6.63	0	45.83	TiO ₂
3	1.01	6.37	27.38	59.45	3.44	0	2.35	Boron oxide
4	1.84	1.41	0	63.90	4.96	0.70	27.19	TiO ₂
5	3.28	3.29	19.44	38.77	28.37	0.62	6.23	Boron oxide
6	0.51	7.37	27.30	57.03	7.16	0	0.64	MgO(B ₂ O ₃) ₂
7	0.02	0.03	32.61	23.09	44.19	0.03	0	B ₂ O ₃

Point	Element (at.%)						
	Al	Mg	B	O	C	Ca	Ti
1	1.67	2.59	61.26	5.00	28.75	0.14	0.59
2	0.62	0.86	0	64.55	12.43	0	21.54
3	0.45	2.49	36.84	49.15	8.27	0.14	2.65
4	1.33	1.14	0	78.04	8.06	0.34	11.09
5	3.12	2.91	22.41	35.72	28.99	0.51	6.34
6	0.45	3.49	36.84	49.15	8.27	0.14	1.64
7	0.01	0.02	37.04	17.72	45.18	0.03	0