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Cyclic oxidation behavior of TiC/Ti_3AlC_2 composites at 550–950 °C in air

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ABSTRACT

Bulk TiC/Ti_3AlC_2 composites containing 5 vol% TiC were fabricated by pressure-assisted self-propagating high-temperature synthesis, and their cyclic oxidation behavior was investigated at 550–950 °C in air for up to 40 cycles. The results demonstrated that at temperatures of 750–950 °C TiC/Ti_3AlC_2 composites displayed excellent cyclic oxidation resistance. The oxidation kinetics basically followed a parabolic rate law. As revealed by XRD and SEM/EDS, the scales consisted of an outer discontinuous layer of rutile TiO_2 and an inner continuous layer of α-Al_2O_3. The scales were dense, adhesive to the substrate and resistant to thermal cycling. However, at lower temperatures of 550 and 650 °C, the oxidation kinetics followed a linear rate law with larger oxidation rates. The cyclic oxidation resistance was deteriorated owing to the formation of microcracks and voids in the scales.

1. Introduction

First identified by Pietzka and Schuster [1] in 1994, the ternary compound Ti_3AlC_2 is a new member of MAX phase materials [2,3] and was found isotropic with the well-known Ti_3SiC_2 [4]. Both theoretical calculations [5,6] and experimental studies [4,7–9] have proved that Ti_3AlC_2 possesses an unusually combined properties of both ceramics and metals. Similar with ceramics, it is oxidation resistant, high-temperature stable up to 1360 °C and light weight with a low theoretical density of 4.247 g/cm^3. Similar with metals, it is an excellent thermal and electrical conductor, readily machinable with conventional tools, and tolerant to damage. These excellent properties render Ti_3AlC_2 many potential applications in diverse fields, especially for high-temperature components.

For high-temperature structural materials, oxidation resistance is an important criterion. The isothermal oxidation properties of Ti_3AlC_2 have been extensively investigated [10–14]. Barsoum developed the oxidation mode of Ti_3AlC_2 and found layered scales after long time oxidation. Zhou et al. concluded that the oxide layer was dense and adherent to Ti_3AlC_2 at high-temperature up to 1300 °C under isothermal-oxidation conditions. However, high-temperature materials are often subject to thermal shock during real applications, which can cause scale cracking and spalling. As a consequence, the scales cannot effectively protect the beneath substrate from further oxidation. Therefore, the cyclic oxidation behaviors of high-temperature materials need special attention. Lee et al. [15] studied the effect of grain size on the cyclic oxidation of Ti_3AlC_2 between 900 and 1200 °C, which was not significant and that the oxide scale was adhesive to Ti_3AlC_2 substrate. Zhou and co-workers [12] pointed out that the oxide scale formed at 1300 °C after 100-time cyclic oxidation was dense and resistant to thermal cycling. However, studies on cyclic oxidation for Ti_3AlC_2 at intermediate temperatures are totally unavailable, as far as known. Therefore, it is necessary to investigate the cyclic oxidation behaviors of Ti_3AlC_2 at intermediate temperatures both for fundamental studies and engineering applications.

In this work, we reported the cyclic oxidation behavior of TiC/Ti_3AlC_2 composites at an intermediate temperature range of 550–950 °C in air. The cyclic oxidation kinetics, phase compositions and morphologies of the scales were extensively studied.

2. Experimental details

Bulk TiC/Ti_3AlC_2 composites used for cyclic oxidation tests were prepared by pressure-assisted self-propagating high-temperature synthesis (SHS). The experimental details can be found elsewhere [16]. By using the Rietveld method [17], phase quantification analysis confirmed that TiC concentration was 5% in volume. Samples were cut into rectangular bars with a dimension of $3 \times 4 \times 30\,\mathrm{mm}^3$ from the central part of the bulk materials by the electrical discharge machining method. All surfaces were polished with a 1200 grit SiC waterproof paper, and followed by ultrasonically cleaning in acetone. The cyclic oxidation experiments were performed using a muffle furnace at 550–950 °C in air for up to 40 cycles. Each cycle of the oxidation experiment composed of heating for 1 h in the muffle furnace at the setting temperature and cooling in air for10 min. Samples were placed in an alumina crucible for quickly taking out and returning to ensure rapid heating and cooling rate. After 10 min cooling in air, the sample was weighed discontinuously by an electronic microbalance with an accuracy of $\pm 10^{-4}$ g.

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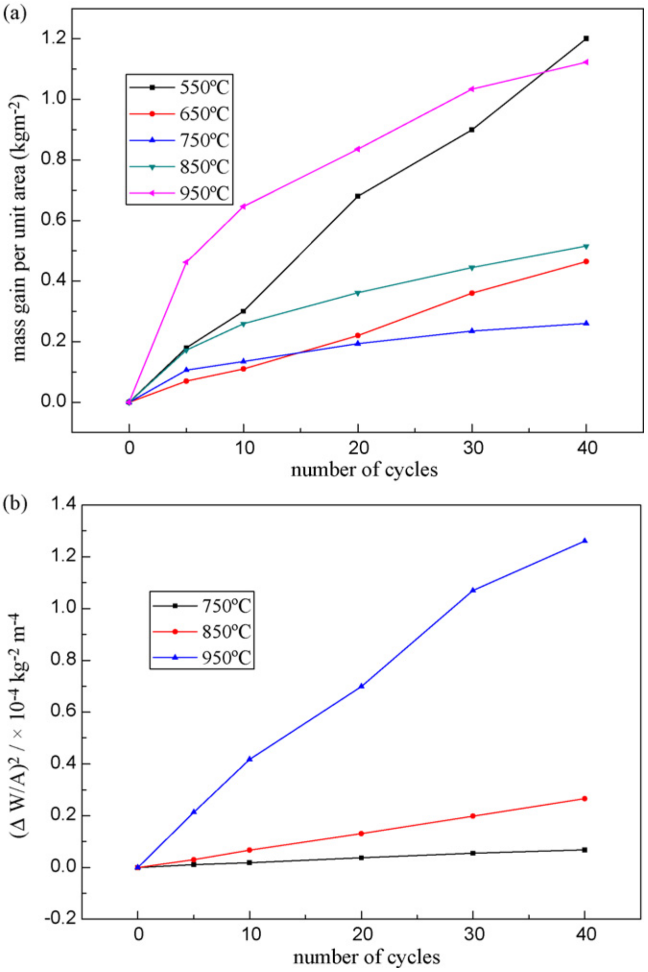

Fig. 1. (a) Plot of mass gain per unit surface area vs. number of cycles for the studied material at 550–950 °C and (b) square of the corresponding mass gain per unit surface area as a function of number of cycles at 750–950 °C.

The phases of the oxidized samples were identified by both X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD was carried out in a D/max-rB diffractometer (Rigaku, Japan) with Cu K_α radiation. The XPS analysis was performed in an ESCA 5700 spectrometer (PHI, USA) using Al K_α X-ray source (1486.6 eV). High resolution spectrum of the Al2p core was recorded. The surface and cross-section microstructures of the oxidized samples were observed in a FEI Sirion 200 scanning electron microscope (SEM; Philips, Netherlands) with a LINK ISIS 300 energy dispersive spectroscopy system (EDS; Oxford Instruments, UK). Prior to the SEM observation, a thin layer of gold was coated on the surface and cross-section of the oxidized samples.

3. Results and discussion

3.1. Cyclic oxidation kinetics

Fig. 1(a) shows the relations between mass gain per unit surface area and number of cycles at 550–950 °C. It can be seen that the mass gain increases slowly at higher temperatures of 750–950 °C as increasing cycle number. Even at the maximum temperature of 950 °C, the final mass gain after 40-cycle oxidation is only 1.1×10^{-2} kg/m^2, which suggests that the studied material has excellent cyclic oxidation resistance. However, a strange phenomenon is found at lower temperatures of 550 and 650 °C. The mass gain per unit surface area for the sample exposed at 550 °C increases quicker than at 650–850 °C with increasing cycles. The final mass gain per unit surface area for the sample exposed at 650 °C is larger than that at 750 °C. This phenomenon indicates that an abnormal oxidation occurred at lower temperatures of 550 and 650 °C, and as will be explained by SEM observation in the following section. Visual inspection indicates that the oxidation kinetics at 550 and 650 °C basically follows a linear rate law. Obviously, it can be concluded that the oxidation resistance of the TiC/Ti_3AlC_2 composites at 550 and 650 °C is poor because of larger mass gains.

The oxidation kinetics of the studied materials at 750–950 °C was examined using a parabolic rate law which assumes that the oxidation rate is controlled by the ion diffusion through the oxide scale. It is well known that for a parabolic rate law, the oxidation kinetics can be written as

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t + c \qquad (1)$$

where $\Delta W/A$ is the mass gain per unit surface area, k_p is the parabolic rate constant, t is the number of cycles, and c is a constant. The square of the mass gain per unit surface area as a function of number of cycles is plotted in Fig. 1(b). It is observed that the $(\Delta W/A)^2$ vs. t plots approximately shows linear shape, confirming that the oxidation kinetics at 750–950 °C follows a parabolic rate law. This suggests that protective oxide scales have formed on TiC/Ti_3AlC_2 composites at 750–950 °C. The change from the linear rate law at lower temperatures, i.e. 550 and 650 °C, to the parabolic rate law at higher temperature of 750–950 °C indicates that the cyclic oxidation mechanism of the studied material changes from a chemical reaction-controlled process to an ion diffusion-controlled process. Obviously, the oxidation rates are not determined simply by temperature.

3.2. Phase constituents of the oxide scale

It is believed that the oxidation kinetics is affected by the oxide species formed on the substrate. Therefore the oxides formed at 550–950 °C after 40-cycle oxidation were first identified by XRD, as shown in Fig. 2. It is interesting to find that each diffraction peak corresponding to Ti_3AlC_2 is visible after 40 cycles at 750–950 °C, indicating that the oxide scales are thin and that there must have formed a protective barrier on the substrate to reduce further oxidation. For the samples exposed at 750–950 °C, the oxide scales all consist of rutile TiO_2 and α-Al_2O_3. However, at 550 and 650 °C, the scales contain two modifications of TiO_2, i.e., anatase and rutile TiO_2. No obvious diffraction peaks corresponding to crystalline aluminum oxides are detected. Generally speaking, because of oxidation, aluminum oxides are believed to exist in the oxide scales. In other words, aluminum oxides formed at 550 and 650 °C are

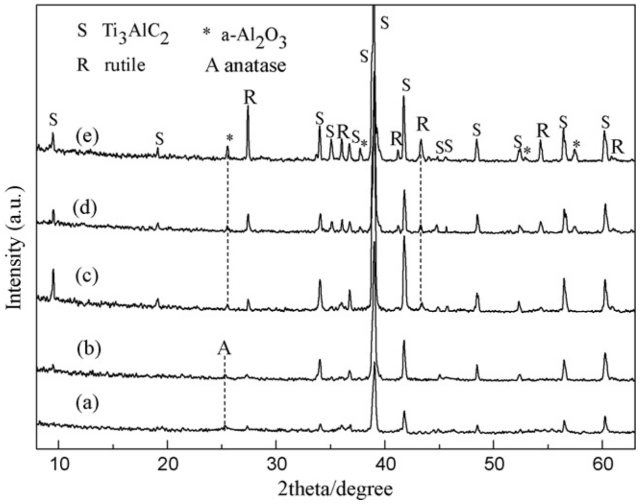

Fig. 2. X-ray diffraction patterns from the oxide scales formed at various temperatures: (a) 550 °C, (b) 650 °C, (c) 750 °C, (d) 850 °C and (e) 950 °C.