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Short communication

Thermal stability of Ti_3AlC_2 in Ar-10vol.%CO atmosphere

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ABSTRACT

Thermal stability of Ti_3AlC_2 at 1250–1400 °C in 10%CO-Ar atmosphere has been investigated. Decomposition of Ti_3AlC_2 occurs when the temperature is 1250 °C. After the treatment at 1300–1400 °C, nanoscale aluminum oxycarbides (Al_2OC and Al_4O_4C) were formed on the sample surface due to the reaction between Al and CO. At 1250–1300 °C, a mixture layer of Ti(O,C) and Al_2O_3 was formed; while at 1350–1400 °C, the reaction scale below the nanoscale aluminum oxycarbides are a duplex layer with a porous Ti(O,C) inner layer and a mixture of Ti(O,C) and Al-containing compounds outer layer. The outward extraction of Al and Ti along some special planes, i.e., {0 0 0 1} and {1 1 −2 0} of Ti_3AlC_2, is believed to result in the orderly arranged pores in the inner porous Ti(O,C) layer.

1. Introduction

$M_{n+1}AX_n$ phase materials (M is a transition metal, A is a III A or IV A group element, and X is either C or N) are excellent candidate materials for many applications due to their unique combination of properties of both metals and ceramics [1–3]. Ti_3AlC_2, one typical representative of the MAX phases, has been well studied for its low density, high electrical and thermal conductivity, high modulus and moderate strength, and good high-temperature oxidation resistance, etc [4–7]. However, calculation on electronic and structural properties of Ti_3AlC_2 showed that the Ti-Al bonds were relatively weaker [8]. This suggests that the thermal stability of Ti_3AlC_2 should be mainly determined by these weak bonds. Recently, first-principle calculation on defects configuration in another similar MAX phase material (Ti_3SiC_2) further showed that it was easier for Ti and Si to diffuse along the basal planes ({0 0 0 1} planes) [9]. But diffusion of Ti and Si atoms along other planes has not been reported yet.

Thermal stability of Ti_3AlC_2 in different atmosphere at high temperatures has been widely investigated, which indicated that it depends strongly on the environment. Wang and Zhou [10] studied the stability of Ti_3AlC_2 in argon and found that nano-laminate Ti_3AlC_2 was stable below at least 1400 °C. By treating in vacuum, Pang et al. [11] reported that Ti_3AlC_2 decomposed above 1400 °C through the sublimation of Ti and Al. Chen et al. [12] reported that Ti_3AlC_2 could decompose at temperature as low as 1150 °C in high vacuum ($\sim 10^{-2}$ Pa). Thermal stability investigation on Ti_3SiC_2 showed that it was stable at 1800 °C under argon atmosphere in a tungsten-heated furnace, but dissociated to TiC_x when using a graphite heater [13], which suggests that carbon containing environment could lower the chemical stability of Ti_3SiC_2.

Our previous work, i.e., synthesis of Al_2OC whiskers by heat treating bulk Ti_3AlC_2 in a carbon-containing environment [14], showed that it might be the formation of CO that accelerates the decomposition of Ti_3AlC_2. Therefore, one aim of this paper is to confirm the effect of CO on the decomposition of Ti_3AlC_2 by treating Ti_3AlC_2 in flowing Ar-10vol.%CO. In addition, this paper can also contribute to the application of Ti_3AlC_2 in CO-containing atmosphere at high temperature.

2. Experimental

Bulk Ti_3AlC_2 material was fabricated by the solid–liquid reaction synthesis and simultaneous in situ hot pressing process [1]. For thermal stability experiments, rectangular samples ($15 \times 5 \times 2\ mm^3$) were cut using an electrical-discharge machining method. The samples were ground, polished and ultrasonically cleaned. The heat treatments were performed in a high temperature furnace in flowing Ar-10vol.%CO (flowing rate is 0.5 l/min) by heating the samples from ambient temperature to 1250–1400 °C at a rate of 8 °C/min and holding for 30 min.

Surface phase compositions after the treatments were identified by X-ray diffractometer (XRD) with Cu Kα radiation (Rigaku D/mac-2400, Japan). The surface and cross-sectional microstructures of the treated samples were observed by the SUPRA35 scanning

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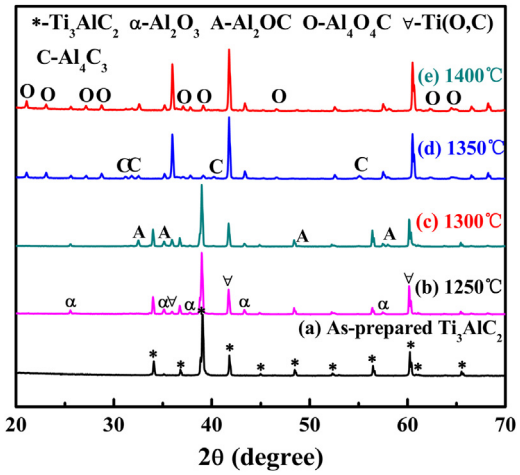

Fig. 1. XRD patterns of samples before and after the treatment at 1250–1400 °C for 30 min.

electron microscope (SEM, LEO, Oberkochen, Germany), equipped with an energy-dispersive spectroscopy (EDS, INCA, Oxford Instrument, Oxford, U. K.) system.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of the sample surfaces before and after the treatments at 1250–1400 °C for 30 min. The as-prepared Ti_3AlC_2 sample is highly pure, as shown in Fig. 1a. After the treatment at 1250 and 1300 °C, Ti_3AlC_2 is still the dominating phase, as shown in Fig. 1b and c. Besides, α-Al_2O_3 and one phase with TiC_x structure were also detected. Considering the existence of CO in the atmosphere, the material with TiC_x structure here should be Ti(O,C). Al_2OC was also formed after the treatment at 1300 °C, which should be attributed to the reaction between Al and CO [15]. While no peak belonging to Ti_3AlC_2 can be detected after the treatment at 1350 and 1400 °C, indicating that the reaction scale is very thick. Beside α-Al_2O_3, Ti(O,C) and Al_2OC, Al_4C_3 and Al_4O_4C were also detected, which might also be attributed to the further reaction between Al and CO.

Table 1
EDS analysis results of the nanoscale materials formed on sample surfaces after treating at 1300–1400 °C.

Element	Al	C	O
1300 °C	47.05	27.90	25.05
1350 °C	48.79	19.79	31.43
1400 °C	49.82	24.98	28.09

The surface morphologies of samples treated at 1250–1400 °C are shown in Fig. 2. Nanoscale materials (NMs) can be found on all the sample surfaces. The amount of NMs becomes larger with the rise of treating temperature. The NMs formed at 1300 °C are two-dimensional sheet-like materials with about 200–300 nm in thickness and more than 50 μm^2 in area, as shown in Fig. 2b. The EDS analysis taken from the sheet-like materials shows that their elemental compositions are Al, O and C and their atomic ratio is close to 2:1:1, as shown in Table 1. Combining the phase composition results in XRD, the sheet-like materials should be Al_2OC. For the samples treated at 1350 and 1400 °C, the elemental compositions of NMs on the surfaces are similar to that formed at 1300 °C, but the phase compositions should contain Al_2OC and some Al_4O_4C because of the higher O content, as shown in Table 1. In addition, Al_4C_3 phase with hydrolytic property was excluded because of the nearly invariant surface morphologies after placing the samples in air for more than one year.

To understand the reaction process, the morphologies and phase compositions of the cross-sections were examined. Fig. 3a and b shows the back-scattered electron images of the fractured specimens treated at 1300 and 1350 °C and the corresponding EDS mapping scan results taken from the region circled by white lines. The results of the sample treated at 1250 and 1400 °C are similar to that treated at 1300 and 1350 °C, respectively, and not shown here for brevity. It can be seen that the reaction layer becomes thicker

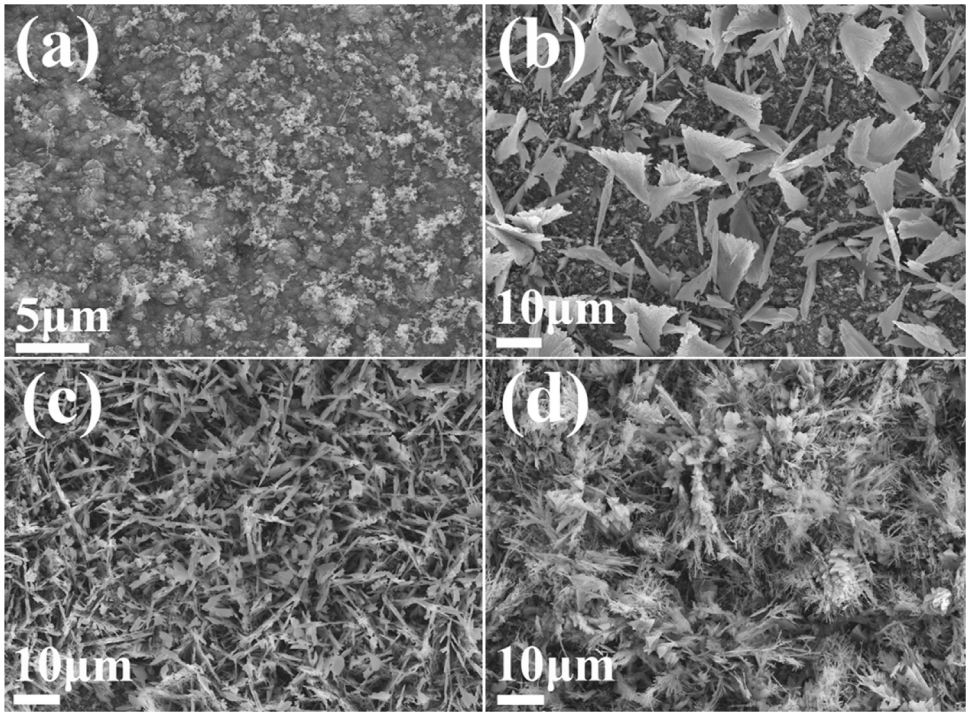

Fig. 2. Surface morphologies of samples after the treatment at (a) 1250 °C, (b) 1300 °C, (c) 1350 °C and (d) 1400 °C.