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Letter

Phase segregation of titanium-aluminium carbide (Ti_2AlC) at high pressure and high temperature

Jiaqian Qin[a], Duanwei He[a,b,*], Chao Chen[a], Jianghua Wang[a], Juan Hu[a], Binwei Yang[a]

[a] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, PR China
[b] Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China

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Abstract

The high pressure and high temperature (HPHT) behavior and phase stability of titanium-aluminium carbide (Ti_2AlC) were investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron micrograph (SEM), and energy-dispersive X-ray analysis (EDXA). The results show that the decomposition temperature of Ti_2AlC decreases against pressure. At pressures of 3, 4 and 5 GPa, the low temperature limits of phase segregation of the sample Ti_2AlC lie between 1300 and 1200 °C, 1100 and 1000 °C, 900 and 800 °C, respectively. The decomposition products are identified to be titanium carbide and titanium aluminium.

Keywords: High pressure and high temperature; Ti_2AlC; Phase segregation

There are more than 50 ternary carbides and nitrides reported with the general formula $M_{n+1}AX_n$ (MAX) [1–3], where $n = 1$, 2 or 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element, and X is C or N. These so-called MAX phase compounds combine some of the best attributes of metals and ceramics: they are machinable, good thermal and electrical conductors, thermal shock resistant, damage tolerant, stiff, and have low thermal expansion coefficients [4–10]. MAX phases such as M_2AlC (M = Ti, Cr, V, Nb, Ta) are expected to have great potential applications as engineering materials.

In the previous studies, the high-pressure behavior of some MAX phases was investigated using diamond anvil cells together with synchrotron X-ray diffraction techniques. Recently, Manoun et al. reported on the high-pressure studies of Ti_3SiC_2 [11], $Ti_3Si_{0.5}Ge_{0.5}C_2$ [12], Zr_2InC [13], Ti_4AlN_3 [14], Nb_2AsC [15], M_2AlC (M = Ti, Cr, V, Nb, Ta) [16], Ta_4AlC_3 [17], Ti_2AlN and Ti_2AlC [18], and Ti_3GeC_2 [19]. In all cases, no phase transformations were observed up to 55 GPa. These works indicate that the MAX phases have good structure stability at high pressure and room temperature. It was also found that the MAX phase compounds maintain stable to 1300 °C at ambient pressure according to the recent studies on Ti_3SiC_2, Ti_3GeC_2, $Ti_3Si_{0.5}Al_{0.5}C_2$, and Ti_2AlC [20].

However, there is no reported work to date concerning the study of high pressure and high temperature (HPHT) influence on the behavior of MAX phases. As these compounds are expected to be used in harsh environments of high stress and high temperature, it is interesting to look at their behavior at simultaneous high pressure and high temperature conditions. In this letter, we report on the phase segregation of Ti_2AlC at HPHT up to 5 GPa and 1400 °C. In addition to it potential technological importance, Ti_2AlC was chosen for study because its structure stability has been examined under high pressure and room temperature as well as at high temperature and ambient pressure conditions [16,18,20].

The structure and fabrication of Ti_2AlC were first reported on in the early1960s by Jeitschko et al. [2]. It has a hexagonal structure (space group $P6_3/mmc$) with lattice parameters $a = 3.06$ Å and $c = 13.67$ Å. In our experiments, we used the lab-synthesized Ti_2AlC as starting material. The synthesized sample was pul-

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* Corresponding author at: Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, PR China.
E-mail address: duanweihe@yahoo.com (D. He).

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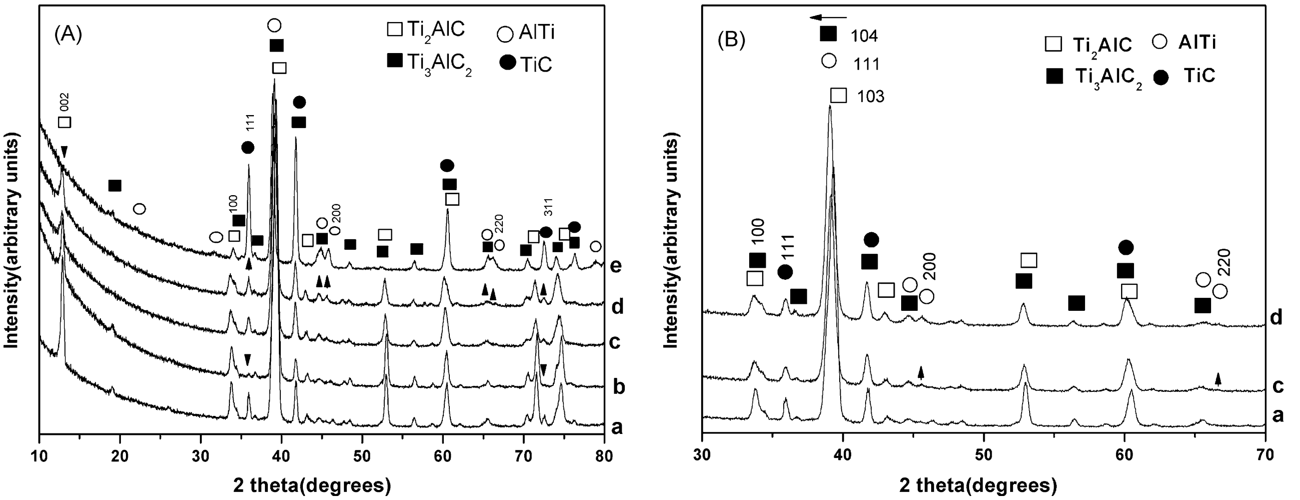

Fig. 1. (A) X-ray diffraction patterns of the selected samples: (a) starting material; (b) sample treated in vacuum at 1300 °C for 20 min; (c) sample treated at 5 GPa and 800 °C for 60 min; (d) sample treated at 5 GPa and 900 °C for 60 min; (e) sample treated at 5 GPa and 1400 °C for 20 min. (B) Enlarged image of the selected area of (a, c and d) in (A).

verized to powder (averaged grain size ∼20 μm) and the X-ray diffraction pattern of the starting material is shown in Fig. 1A(a). Besides the main phase of Ti_2AlC, the starting samples also contain two minor phases (TiC and Ti_3AlC_2). The purity of the Ti_2AlC powder is estimated to be larger than 95% according to the XRD examination. The powder was pre-compressed (∼200 MPa) into discs (8 mm diameter and 4 mm height). The starting sample discs were placed into hexagonal boron nitride capsules for HPHT treatments.

High pressure and high temperature experiments were carried out with a DS6 × 8MN cubic press. The sample temperature in the high-pressure cell was measured directly using a PtRh6%–PtRh30% thermocouple. The cell pressure is estimated by the oil pressure reading, which has been calibrated with the method of silver melting point at high pressure [21]. The sample was first pressurized to a desired pressure, and then heated to a high temperature. After keeping these high pressure–temperature (*P*–*T*) conditions for 20 or 60 min, the samples were quenched to room temperature and then decompressed to ambient pressure. The HPHT-treated samples are usually well sintered. All the recovered samples were carefully grinded and polished before examined by X-ray diffraction (XRD), scanning electron micrograph (SEM), and energy-dispersive X-ray analysis (EDXA).

Fig. 1A shows the X-ray diffraction patterns of the starting material and the selected samples treated at high pressure–temperature conditions. One of the samples was treated in vacuum at 1300 °C for 20 min to confirm the thermal stability of the Ti_2AlC phase as shown in Fig. 1A(b). It can be seen that the sample treated in vacuum at 1300 °C for 20 min has a similar XRD pattern to that for the starting material (Fig. 1A(a)), but the intensity of characteristic diffraction peaks of TiC (1 1 1) and TiC (3 1 1) decrease obviously (marked by arrow in Fig. 1A(b)). The thermal stability of the Ti_2AlC phase was also checked up to 1500 °C in vacuum by differential scanning calorimetry (DSC) with the heating rate of 20 K/min. Except for a small peak in the DSC curve (unpresented) at 900–1000 °C, no more peak was observed. Based on the DSC and XRD data for the sample treated in vacuum at high temperature, we think that there was a reaction of $Ti_2AlC + TiC \rightarrow Ti_3AlC_2$ happened at high temperature of about 950 °C in vacuum, and the Ti_2AlC phase can maintain stable at high temperature at least up to 1500 °C in vacuum.

There is no difference between the XRD pattern of the HPHT-treated sample at 5 GPa and 800 °C for 60 min (Fig. 1A(c)) and that of the starting material (Fig. 1A(a)). After the sample was treated at 5 GPa and 900 °C for 60 min as shown in Fig. 1A(d), some minor changes were observed by XRD, and the further phase identification shows that a AlTi (PDF #65-0428) compound formed in the sample. The intensity of diffraction peaks of AlTi and TiC was found to increase (marked by arrow in Fig. 1A(d)) with temperature for the samples treated at 5 GPa and high temperature above 900 °C. To make it clear, the enlarged image of the selected area in Fig. 1A(a, c and d) are shown in Fig. 1B. After treating at 5 GPa and 900 °C for 60 min, we can find new peaks (AlTi diffraction peaks) started to appear in Fig. 1B(d) (marked by arrow), but no AlTi diffraction peaks appear in Fig. 1B(c). The intensity of AlTi diffraction peaks has been found to increase with the temperature, and more AlTi diffraction peaks are observed for the sample treated at 5 GPa and 1400 °C (Fig. 1A(e)). According to the XRD data, Ti_2AlC has decomposed completely at 5 GPa and 1400 °C, and we can conclude that the reaction for the formation of AlTi is $Ti_2AlC \rightarrow AlTi + TiC$ under high pressure and high temperature.

If the above phase segregation of Ti_2AlC occurs at HPHT, TiC will separate out and the relative intensity of TiC (1 1 1) and Ti_2AlC (1 0 0) will be changed. As compared to Fig. 1B(a), the relative intensity of TiC (1 1 1) and Ti_2AlC (1 0 0) in Fig. 1B(c) did not change, this indicates that no phase transformations happened for Ti_2AlC at 5 GPa and 800 °C. But the intensities of TiC (1 1 1) and Ti_2AlC (1 0 0) peaks in Fig. 1B(d) became almost identical. Thus, the phase segregation of Ti_2AlC occurred at