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Synthesis reactions for Ti_3AlC_2 through pulse discharge sintering TiH_2/Al/C powder mixture

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Abstract

Ternary compound Ti_3AlC_2 was synthesized through pulse discharge sintering (PDS) the powder mixture of TiH_2/Al/C without preliminary dehydrogenation. The synthesis mechanism of Ti_3AlC_2 was revealed to be completed via the reactions among the intermediate phases of Ti_3Al, $TiAl_3$, TiAl, TiC and Ti_2AlC, as well as the starting reactants. In comparison with the materials synthesized from TiH_2/Al/TiC or Ti/Al/C powder mixtures, more impurity phases were found in the synthesized Ti_3AlC_2. Analysis of the sintering curves as well as the intermediate phase formation during the reactive sintering process revealed that incomplete dehydrogenation of TiH_2 postponed the formation of intermediate phases, which in turn resulted in final products with more impurity phases.

Keywords: Ti_3AlC_2; Pulse discharge sintering (PDS); Synthesis; TiH_2; Dehydrogenation

1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) is a novel material which belongs to the so-called "312" ternary carbides material group (i.e. Ti_3SiC_2, Ti_3AlC_2, Ti_3GeC_2) [1–6]. Similar to Ti_3SiC_2, Ti_3AlC_2 is a remarkable material that combines many of the best attributes of both metals and ceramics, such as low density (4.25 g/cm^3), high modulus, high strength at high temperatures, readily machinable, non-susceptibility to thermal shock, good oxidation resistance, high electrical conductivity [2–5]. Its Young's modulus is about 297 GPa and shear modulus is about 124 GPa [2]. It has high compressive strength at both room and high temperatures, with its failure mode below 1000 °C being by shear fracture, while above 1050 °C the deformation is ductile [3]. Meanwhile, Ti_3AlC_2 has excellent oxidation resistance by forming adhesive continuous Al_2O_3 layer on Ti_3AlC_2 surface at higher temperature [3].

The synthesis of Ti_3AlC_2 was first reported in 1994 by Pietzka and Schuster through sintering cold-compacted powder mixtures of titanium, TiAl, Al_4C_3 and carbon at 1300 °C in H_2 atmosphere for 20 h [7]. However, the purity and relative density were not reported because this work emphasized the phase equilibrium in the ternary system. In 2000, Tzenov and Barsoum reported that polycrystalline bulk samples of Ti_3AlC_2 have been fabricated by reactively hot isostatic pressing (HIP) a mixture of titanium, graphite and Al_4C_3 powders at a pressure of 70 MPa and temperature of 1400 °C for 16 h [2]. This is believed to be the first synthesis of fully dense bulk Ti_3AlC_2. In recent years, hot-pressing (HP) [3–5,8,9], self-propagating high temperature synthesis (SHS) [10–12] and pulse discharge sintering (PDS) [5,6,13,14] were employed to synthesize Ti_3AlC_2. In these processes, it is noted that most sintering processes employed metallic Ti powder as a starting material. The report of TiH_2 powder as a reactant is limited [14]. TiH_2 powder is the intermediate product during the fabrication processes for crushed metallic Ti powder, so that it is lower in cost than metallic Ti powder. The market price of TiH_2 powder is about half of metallic Ti powder with equivalent particle size. Therefore, to bring this fascinating ternary compound closer to application with lower cost, the synthesis of Ti_3AlC_2 from TiH_2 powder is a practical attempt. In general, however, when employing TiH_2 powder as the reactant for synthesizing MAX phases,

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the long annealing time was believed to be necessary for preliminarily removing hydrogen in TiH_2 [15,16]. For example, it is reported that the powder mixture containing TiH_2 were annealed at 900 °C for 6 h to remove hydrogen prior to powder blending for synthesizing Ti_3SiC_2 [15]. In our previous study, single-phase dense Ti_3AlC_2 was rapidly synthesized by PDS of the powder mixture of TiH_2/Al/TiC without preliminary dehydrogenation [14]. The dehydrogenation and synthesis reactions were successfully incorporated in a single run of reactive sintering process for Ti_3AlC_2 synthesis. However, the synthesis of Ti_3AlC_2 using powder mixture of TiH_2/Al/C at even lower cost has never been reported. One possible difficulty for using this reaction system is that the whole Ti in Ti_3AlC_2 needs to be provided from TiH_2 (in the TiH_2/Al/TiC system, two third of Ti was contributed from TiC). This requires more TiH_2 as reactant than that of TiH_2/Al/TiC, consequently dehydrogenation becomes more important during the synthesis process. The objectives of the present work are to explore the possibility of synthesizing Ti_3AlC_2 by PDS process from TiH_2/Al/C powder mixture without preliminary dehydrogenation, and to understand the mechanism of the Ti_3AlC_2 formation.

2. Experimental procedure

Starting powders (all from Kojundo Chemical Lab. Saitama, Japan) of TiH_2 (−45 μm, 99%), Al (−10 μm, 99.9%), and C (5 μm, 99%), were used in this study. The powders were mixed in molar ratio of TiH_2: Al:C = 3:1.1:1.8 (Ti:Al:C = 3:1.1:1.8). This slightly off-stoichiometric composition was selected according to the literature and our previous work [2,3,17], by which single-phase Ti_3AlC_2 was synthesized. These powders were mixed in a Turbula shaker mixer in Ar atmosphere for 24 h. The powder mixture was filled in a graphite mold (20 mm in diameter) and sintered in vacuum by using PDS technique (PAS-V, Sodick Co. Ltd.). The sintering temperature was monitored and controlled through an infrared camera. The heating rate was controlled at 50 °C/min, and the sintering temperature was selected in the range of 900–1500 °C and held at these temperatures for 0–60 min. The powder compact was kept under a constant axial pressure of 50 MPa during sintering. After sintering, the samples were ground to remove surface layer for 1 mm in order to eliminate the carbon effect. Then the samples were analyzed by X-ray diffractometry (XRD) with Cu Kα radiation at 30 kV and 40 mA to identify the phase constitution. In order to avoid the effect of preferred orientation, powder samples were taken by drilling into the bulk of the samples for analysis of phase contents by XRD. The microstructure of the synthesized samples were observed and analyzed by using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system. For the SEM observation, the samples were mechanically polished and etched in a solution of H_2O:HNO_3:HF (2:1:1).

3. Experimental results

3.1. X-ray diffraction (XRD)

Fig. 1 shows the XRD patterns of the samples sintered in the temperature range of 1250–1500 °C for 20 min. After sintering at 1250 °C for 20 min, three phases were confirmed, i.e. Ti_3AlC_2, Ti_2AlC and TiC phases. This indicates the formation of Ti_3AlC_2 at this temperature, although the dominating phase is Ti_2AlC at this temperature. With an increase in sintering temperature, the relative intensity of Ti_2AlC and TiC decreased gradually. When the sample was sintered at 1450 °C for 20 min, the intensity of Ti_3AlC_2 dominated in the pattern. However, when the sintering temperature was increased to 1500 °C, the relative intensity of Ti_3AlC_2 in the XRD pattern decreased considerably. This indicates that the Ti_3AlC_2 is not stable above 1450 °C.

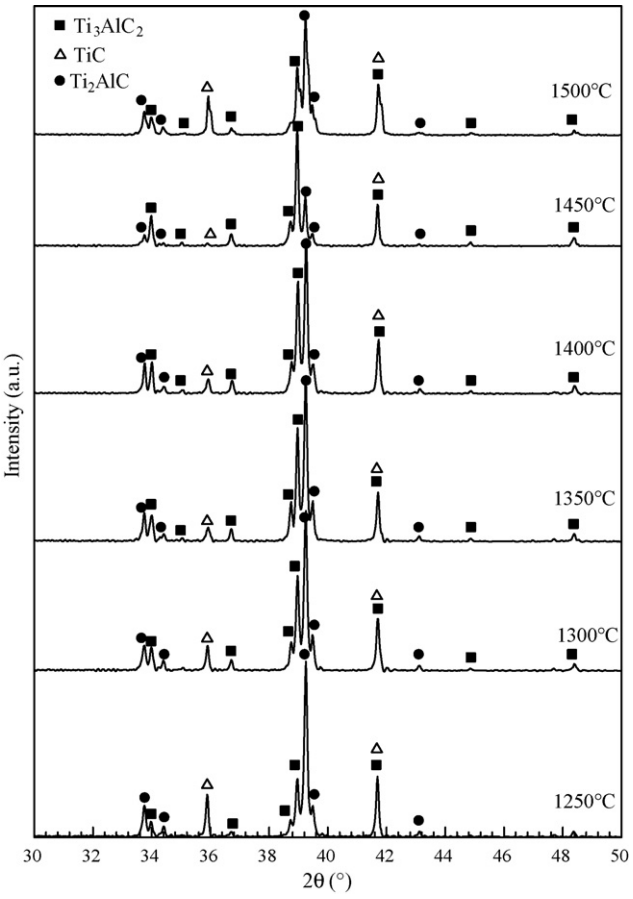

Fig. 1. X-ray diffraction patterns of the TiH_2/Al/C powder compacts sintered at various temperatures for 20 min.

Fig. 2 shows the XRD patterns of the samples sintered in the temperature range of 1300–1450 °C for 60 min. These results showed that extending the sintering time at different temperatures did not improve the content of Ti_3AlC_2 obviously. The relative intensities of Ti_3AlC_2 main peaks are even lower than those sintered for 20 min at 1450 °C. This might be attributed to the poor thermal stability of Ti_3AlC_2 at this temperature. In other words, the Ti_3AlC_2 synthesized at this temperate decomposed with an increase in the soaking time.

3.2. Content of Ti_3AlC_2

The contents of the constituent phases of Ti_3AlC_2, Ti_2AlC and TiC in the synthesized products can be estimated from the integrated XRD peak intensities according to the following equations [18]:

$$W_a = \frac{I_a}{I_a + 0.220 I_b + 0.084 I_c} \quad (1)$$

$$W_b = \frac{I_b}{4.545 I_a + I_b + 0.382 I_c} \quad (2)$$