Materials Science and Engineering B 173 (2010) 126–129

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Microstructural evolution during the formation of Ti_3AlC_2

Michiyuki Yoshida*, Yasuhiro Hoshiyama, Junji Ommyoji, Akira Yamaguchi

Okayama Ceramics Research Foundation, 1408-15, Nishikatakami, Bizen-shi, Okayama 705-0021, Japan

ARTICLE INFO

Article history:
Received 12 June 2009
Received in revised form
18 December 2009
Accepted 4 January 2010

Keywords:
Ti_3AlC_2
Layered carbide
Microstructure
Reaction mechanism

ABSTRACT

A layered ternary carbide Ti_3AlC_2 was synthesized by pressureless calcining process from the mixture of Ti/Al/2TiC. Almost single phase Ti_3AlC_2 was obtained after calcining at 1400 °C for 1 h. The microstructural evolution during the formation of Ti_3AlC_2 was examined at the temperature from 900 °C to 1400 °C. Based on the results of X-ray diffractometry (XRD) and energy-dispersive X-ray spectroscopy (EDS), a possible reaction mechanism was proposed to explain the formation of Ti_3AlC_2. Above the melting point of aluminum, liquid Al reacts with titanium to form the intermetallic compound of AlTi. As the temperature is increased to 1400 °C, the intermetallic compound of AlTi reacts with TiC to form Ti_2AlC and then, Ti_2AlC further reacts with TiC to form the final product of Ti_3AlC_2.

1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) is one of the three ternary compounds existing in Ti–Al–C system. Ti_3AlC_2, which belongs to a family of layered ternary compounds, has attracted increasing attention owing to their unique combinative properties of both ceramics and metals [1–6]. Like metals it is thermally and electrically conductive, easy to be machined with conventional tools and resistant to thermal shock. Like ceramics it is light weight, elastically stiff, thermal stability, and retains its strength to high temperature.

Since Pietzka and Schuster [7] first reported the synthesis of Ti_3AlC_2 by sintering cold-compacted powder mixtures of Ti, TiAl, Al_4C_3, and C at 1300 °C in H_2 (g) for 20 h, different starting materials and processes have been attempted to synthesize Ti_3AlC_2 [8–13]. Especially, the mixture of elemental Ti, Al and C has been employed for the synthesis of Ti_3AlC_2 by many researchers due to the low processing cost [8–10]. Ti_3AlC_2 exists in complex ternary systems in which several quite stable binary and other ternary phases coexist [7]. The single phase Ti_3AlC_2 is very difficult to synthesize because of its very narrow phase range in Ti–Al–C ternary phase diagram. In recent years, Ge et al. [11] reported that the addition of TiC to starting mixture was beneficial for the formation of the ternary phase Ti_3AlC_2. Peng et al. [12] fabricated high pure Ti_3AlC_2 powder by the pressureless calcination from the mixture of Ti/Al/2TiC. However, the detailed reaction mechanism during the synthesis of Ti_3AlC_2 from the mixture of Ti/Al/2TiC is unknown. In the present study, the mixture of Ti, Al and TiC was chosen to study the reaction mechanism during the formation of Ti_3AlC_2. The purpose of present study is to elucidate reaction mechanism by studying the microstructure during the formation of Ti_3AlC_2.

2. Experimental procedure

TiC (<2 μm powder size, Wako Pure Chemical Industries, Ltd., Japan), Ti (<40 μm powder size, 99% purity, Mitsuwa Chemicals Co., Ltd., Japan), Al (<40 μm powder size, 99% purity, Mitsuwa Chemicals Co., Ltd., Japan) and graphite powders (<5 μm powder size, 99% purity, Kojundo Chemical Laboratory Co., Ltd., Japan) were used as starting materials in this study. The starting materials, with stoichiometric molar ratio of Ti/Al/2TiC and 3Ti/Al/2C, were mixed in ethanol by mechanical stirring for 1 h. After drying, cylindrical compacts: ϕ15 mm × 5 mm were prepared under the pressure of 20 MPa, followed by cold-isostatically pressing (CIP) at 100 MPa. Calcination was carried out in the graphite furnace under Ar-atmosphere (Model FVPHP-R-5, Fujidenpa Kogyo Co. Ltd., Osaka, Japan). The heating rate was controlled at 10 °C/min, and calcining temperature was selected in the range of 900–1400 °C and held for 0–60 min. Phase analysis of pulverized samples was performed by XRD (Model RINT2200, Rigaku Co., Tokyo, Japan) with Cu K_α radiation at 40 kV and 40 mA. For microstructural observation, the synthesized bodies were incorporated into epoxy resin and mechanically polished (1 μm diamond finish). The microstructure of carbon coated samples was observed with scanning electron microscope (Model JSM6490, JEOL, Japan), and energy-dispersive X-ray spectroscopy (Model Genesis2000, EDAX, USA).

* Corresponding author at: Department of Materials Science and Technology, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu City 501-1193, Japan. Tel.: +81 58 293 2566; fax: +81 58 293 2794.
E-mail address: myoshida@gifu-u.ac.jp (M. Yoshida).

0921-5107/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2010.01.006

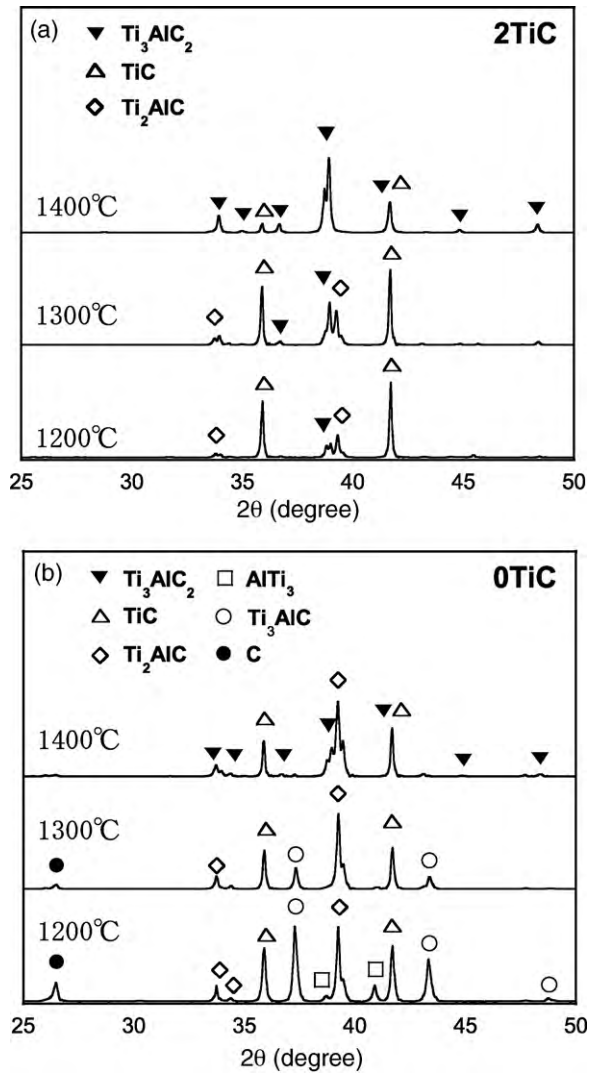

Fig. 1. XRD patterns of the samples heated at 1200–1400 °C for 1 h. (a) The mixture of Ti/Al/2TiC and (b) the mixture of 3Ti/Al/2C.

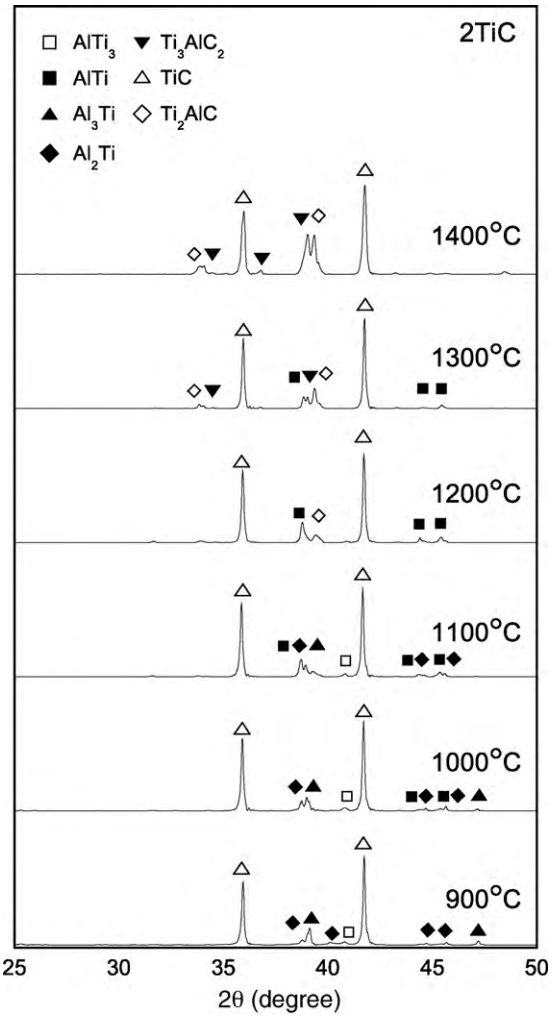

Fig. 2. XRD patterns of the Ti/Al/2TiC powder mixture heated to 900–1400 °C for 0 min.

3. Results and discussion

3.1. XRD results of the calcined samples

Fig. 1(a) shows the X-ray diffraction profiles of the calcined samples prepared from the mixture of Ti/Al/2TiC (abbreviate as "2TiC") heated at the temperature from 1200 °C to 1400 °C for 1 h. When 2TiC sample was heated at 1200 °C, the peaks of TiC, Ti_2AlC and Ti_3AlC_2 were detected. With increasing temperature, the intensity of TiC decreased, while the intensity of Ti_3AlC_2 increased. When 2TiC sample was heated at 1400 °C, the peaks of Ti_2AlC disappeared, and the dominant peaks were Ti_3AlC_2. For a comparison, the XRD profiles of the sample prepared from the mixture of 3Ti/Al/2C (abbreviate as "0TiC") were shown in Fig. 1(b). When 0TiC sample was heated to 1200 °C for 1 h, the peaks of unreacted graphite, $AlTi_3$, TiC, Ti_3AlC and Ti_2AlC were detected. With increasing temperature, the relative intensity of Ti_3AlC, TiC, $AlTi_3$ and graphite decreased. When the sample was heated to 1400 °C, the peaks corresponding to Ti_3AlC_2 appeared. The dominant peaks at 1400 °C were Ti_2AlC and TiC. A lot of intermediate products ($AlTi_3$, Ti_3AlC, TiC and Ti_2AlC) were observed during the synthesis of Ti_3AlC_2 from the 0TiC powder. In the case of 2TiC, the peaks corresponding to Ti_3AlC_2 were observed at lower temperature than those observed in 0TiC. The relative intensity of Ti_3AlC_2 for the 2TiC sample heated at 1400 °C was higher than that for the 0TiC sample. Our results showed that the addition of TiC powder to the starting mixture was beneficial to the formation of Ti_3AlC_2.

Fig. 2 shows X-ray diffraction profiles of 2TiC heated to, and then immediately cooled down from 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C, respectively. The dominant peaks corresponding to unreacted TiC phase were detected at all temperatures. When the sample was heated to 900 °C, the peaks of the intermetallic compounds Al_3Ti, Al_2Ti and $AlTi_3$ were detected. When the temperature was increased to 1100 °C, the intermetallic compound of AlTi appeared. When the sample was heated to 1200 °C, the peaks of Al_3Ti, Al_2Ti and $AlTi_3$ disappeared, and the observed peaks for intermetallic compound were AlTi only. The main peak of Ti_2AlC at about $2\theta = 40°$ appeared at the temperature of 1200 °C. When heated to 1300 °C, the peaks of Ti_3AlC_2 appeared. With increasing the temperature to 1400 °C, the relative intensity of Ti_3AlC_2 and Ti_2AlC increased. According to the XRD results, the main reactions during the formation of Ti_3AlC_2 can be expressed as follows:

$$Al + Ti = AlTi \quad (1)$$

$$AlTi + TiC = Ti_2AlC \quad (2)$$

$$Ti_2AlC + TiC = Ti_3AlC_2 \quad (3)$$