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Original Article

Investigation of Ti_2AlC formation mechanism through carbon and TiAl diffusional reaction

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ABSTRACT

Ti_2AlC formation mechanism with carbon and TiAl alloy as reactants at 1000–1200 °C have been investigated through Raman spectrometer and transmission electron microscope (TEM). Reaction products TiC_x and Ti_2AlC are confirmed. Full width at half height (FWHH) of Ti_2AlC Raman peak is used to characterize crystallinity, which indicates better perfection of Ti_2AlC grains near TiAl area and with higher reaction temperature. Variations of TiC_x microstructure, especially stacking faults(SF) and nanotwins, are observed by TEM along reaction layer. Ti_2AlC lattice uniformity of different reaction temperature is also confirmed by TEM, which is consistent with Raman result. TiC_x is believed first formed through reaction between TiAl and C. With help of carbon vacancy, Al-doped TiC_x SF and nanotwin can be formed under hot pressing, which becomes the basal frame of Ti_2AlC.

1. Introduction

MAX phases with their composition of $M_{n+1}AX_n$ (the space group P63/mmc), where M is transition metal element, A is A-group (mostly IIIA, IVA) element, and X is C or N, have attracted attention because of their unique properties, which combines high electric and thermal conductivities with relatively low hardness, good machinability due to their anisotropy [1–7]. In all these MAX compounds, near-close-packed transition metal carbide and/or nitride layers ($M_{n+1}X_n$) are interleaved with layers of pure A-group element stacking along [0001] direction. In recent studies, $M_{n+1}X_n$ were found as powerful 2D materials. $M_{n+1}X_n$ can be easily harvested by MAX phase etching which reveals specific industrial future [8–15]. Among the MAX phases reported so far, Ti_2AlC is one of the most light-weighted and oxidation resistant [9–11]. In previous reports, bulk Ti_2AlC materials were synthesized through mixture of Ti, Al and graphite powder under high temperature. Wang et al. [16] developed the solid-liquid reaction method in which in situ hot pressing process was operated at 1400 °C to fabricate polycrystalline Ti_2AlC from the stoichiometric elemental powder compact. They concluded that phase purity is highly dependent on the molar ratio of raw powders. Meanwhile, compounds (e.g. TiC, Al_4C_3) or/and pretreatment method, e.g. mechanical milling, are used to decrease sintering temperature and increase reaction conversion rate. Yeh and Shen [17,18] performed systematical study on formation of Ti_2AlC (Ti_3AlC_2) by combustion synthesis. They indicated that addition of TiC and Al_4C_3 led to a decrease at the reaction temperature compared with the elemental reactants. TiC was also found to facilitate the formation and therefore enhance the extent of Ti_2AlC conversion. In another combustion synthesis study, it was indicated that addition of TiAl significantly reduced the combustion temperature and improved Ti_2AlC purity [19,20].

In studies above, synthesis of Ti_2AlC always uses elemental or/and compound powders as reactants, which prevents observation of elemental diffusion reaction process and microstructural evolution. Therefore, reaction mechanism of Ti_2AlC synthesis is still ambiguous. When particle size overwhelms element diffusion ability, particles would not take part in chemical reaction completely so that purity of reaction products decreases. What is worse, Ti and Al powder can constitute many kinds of byproduct (e.g. TiAl, Ti_3Al, $TiAl_3$) at MAX phase synthetizing temperature, which results in impurity in final product (binary carbides and different kinds of MAX phases) [7,17,18] and makes reaction route analysis difficult. Different from element powder, TiAl alloy has specific crystallographic structure so that proportion and atom positions of Al and Ti in unit cell is almost the same in the whole bulk materials, which reduces composition deviation. In addition, previous work indicated that TiAl could be used to synthesize Ti_2AlC [21].

In this work, carbon coated gamma-TiAl alloy samples are used as diffusion reactants at temperature from 1000 to 1200 °C to synthesize Ti_2AlC so that relatively flat and homogeneous reaction interface can be achieved to reveal diffusional reaction process. Reaction products (byproducts) and microstructural evolution during Ti_2AlC synthesis are

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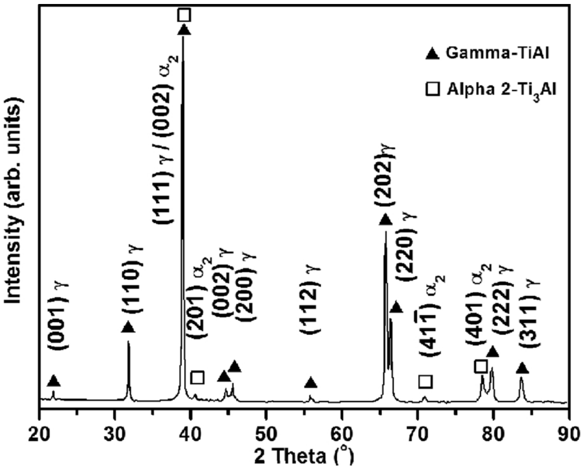

Fig. 1. XRD result of original gamma-TiAl.

investigated. Since conventional x-ray diffraction (XRD) methods, as introduced in many researches above, can hardly be used to analyze layer-like microstructure in scale of micrometer or even smaller, Raman spectrometer is chosen instead due to its high spatial resolution (spot size about 1 μm in diameter), efficiency, as well as little sample preparation requirement. At the same time, TEM is also used to testify Raman characterization and further study fine microstructure of the reaction products.

2. Experiment

TiAl bulk (nominal element content Ti-48Al-1.5Cr) was cutted to pieces of slice (with area of 1.5 cm *1 cm, 3 mm in thickness). XRD of original TiAl microstructure is shown in Fig. 1. Then slices were grinded and polished for carbon deposition. Pyrolytic carbon (thickness about 3–4 μm) coated TiAl alloy slices were hot pressed under vacuum condition at 1000–1200 °C, with the calculated pressure of 200 MPa for 1.5 h, respectively to investigate diffusion reaction. TEM samples were prepared by using crosssection slice of the processed coating sample. Grinding and Argon ion polishing (Gatan 691) were used as final thinning methods. TEM measurement was performed using field emission TEM (FEI Tecnai G2, operating at 200 keV). Raman studies were carried out on a Raman spectrometer (Renishaw InVia, Old town, Gloucestershire, UK) equipped with a 532 nm laser device. The laser beam was focused in air at normal incidence on a small spot area (diameter about 1 μm) of the polished sample crosssection. Raman spectra were obtained with laser power of 5 mW to avoid local heating.

3. Results and discussion

Thickness of reaction layer under different temperature is shown in Table 1. It is obvious that higher reaction temperature is beneficial to element diffusion and chemical reaction proceeding, which results in thicker reaction layer than that of low temperature.

3.1. Raman results of the reaction products

Raman spectra collected along reaction product layer after different temperature treatment reveal varied features (see Fig. 2). The spectra close to carbon coating are similar to that of Fig. 3(a) which show no intense peak but a double hump in the range of 200–400 cm^{-1} and another wider hump in the range of 550–750 cm^{-1}. Compared with Raman spectra of the reported TiC_x for x = 0.86, 0.9, 0.97 and 0.67, it is confirmed that spectrum in Fig. 3(a) belongs to TiC_x [22–24]. Therefore, reaction product near carbon coating is TiC_x. According to previous reports, Stoichiometric TiC has NaCl structure, whose crystal symmetry has no Raman active vibrational modes. It is believed that defects could affect intrinsic crystal symmetry, which may result in unexpected activation of vibrational modes [22]. Therefore all Raman characters obtained in TiC_x are actually disorder-induced.

Table 1
Thickness of reaction layer under different synthesis temperature.

Temperature (°C)	1000	1100	1200
Thickness (μm)	2.5-3.5	3.5-4	5-5.5

Spectrum of Fig. 3(c) mostly appears in the area near TiAl alloy especially ones after higher temperature reaction (e.g. 1100 and 1200 °C). It contains two sharp peaks located at about 260 and 360 cm^{-1} respectively, which is identical to Raman spectrum of Ti_2AlC [2,4,5]. Bulk Ti_2AlC has four Raman active modes, w1 at 136–150 cm^{-1} (E_{2g}), w2 and w3 at about 260–270 cm^{-1} (Peak 1) are assigned to E_{1g} and E_{2g} mode, w4 at about 360–365 cm^{-1} (Peak 2) is assigned to A_{1g} [2]. According to previous reports, the E_{2g} mode-related peak at 136–150 cm^{-1} could not be observed in most experiments including this work [2,4]. Other spectra collected in Raman linescanning are similar to that in Fig. 3(b), with two peaks emerge at about 260 and 360 cm^{-1} of lower intensity and increased FWHH compared with spectrum of Fig. 3(c), and a hump located in the range of 600–750 cm^{-1}, which seems like mixed features of TiC_x and Ti_2AlC. All Ti_2AlC intrinsic Raman modes are involved with vibration of Ti-Al bonding [2]. Previous report indicates the 600–750 cm^{-1} hump is related to Ti-C bonding vibration (for example in Ti_3AlC_2), while this kind of vibration can not be found in bulk Ti_2AlC but in defective ones [2,5]. Naguib et al. [5] confirmed that Raman feature of partially etched Ti_2AlC reveals peak shift and appearance of a big hump in the range of 600–750 cm^{-1}, similar with that observed in this work. Chemical attack can etch away Al atoms in Ti_2AlC lattice, which leads to formation of TiC_x twin structure. Therefore, Raman feature of this defects-related hump could be related to imperfection of Ti_2AlC lattice.

In this work, Raman features of Peak 2 (at about 360 cm^{-1}, A_{1g} mode) is chosen to investigate microstructural variations. After peakfitting of Raman spectra, FWHH and corresponding peakshifts of Peak 2 along reaction layer are shown in Fig. 4. The tendency is obvious that from carbon coating (0 μm position) to TiAl, Peak 2 FWHH decreases while peakshifts increase. Meanwhile when reaction temperature increases (from Fig. 4(a) to (c)), Peak 2 feature changes along reaction product layer become much smoother. According to previous reports, Raman FWHH broadening is related to crystal imperfection [25,26]. In bulk materials, only the Brillouin zone-center (q = 0) optical phonons are observed by Raman spectrometer. However microstructural defects can result in a progressive relaxation of the q = 0 selection rule which contributes to phonon modes away from Brillouin zone center [26–28]. This gives the observed broadening and peakshifts in Raman spectra. Thus Ti_2AlC crystal perfection increases continuously from area near carbon coating to that near TiAl alloy along the reaction layer according to FWHH variation. At the same time, when FWHH increases, intensity of the wide hump at the range of 500–750 cm^{-1} increases as well. As mentioned above, the hump intensity is also related to crystal perfection. Relationship between Peak 2 FWHH and intensity ratio of Peak 2 and the wide hump (under different reaction temperature) is shown in Fig. 5. it is clear that FWHH is proportional to the intensity ratio. When intensity ratio is 0, the measured area is composed of Ti_2AlC, while it becomes 1, the measured area is composed of TiC_x. The lower intensity ratio data are always collected from area near TiAl alloy and under higher reaction temperature, which represents better lattice perfection of Ti_2AlC.

3.2. TEM results of reaction products

Raman results can efficiently provide phase distribution and microstructure evolution of reaction product. However, limited spatial