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THERMAL PROPERTIES OF VARIOUS Ti-Al-C COMPOSITES PREPARED BY HOT SHOCK COMPACTION UTILIZING COMBUSTION SYNTHESIS**WŁAŚCIWOŚCI TERMICZNE KOMPOZYTÓW Ti-Al-C UZYSKANYCH Z WYKORZYSTANIEM METODY UDAROWEGO ZAGĘSZCZANIA NA GORĄCO**

Hot shock compaction method was utilized for the consolidation of MAX phase composites consisting of Ti, Al and C. This paper presents the production of dense, crack-free composites by combining the combustion synthesis with explosive detonation. Another objective is to investigate various properties of the obtained shock-compacts. The shock compacted materials were post-annealed at 1173 K for releasing the shock-induced strain. As a result, these compacts had strong interparticle bonding strength and few macro cracks. Intermetallic compounds (TiAl, Ti₂Al and Ti₃Al) and non-oxide ceramics (TiC and Ti₄Al₂C₂) were detected in as-synthesized and annealed materials by X-ray diffraction experiments. Also, lamella structures of Ti₄Al₂C₂ phase were observed by SEM. It was known that the coefficient of thermal expansion increased with increasing temperature, and decreased with increasing TiC content.

Keywords: underwater-shock compaction, lamella structures, MAX phase, coefficient of thermal expansion

Metodę udarowego zagęszczania na gorąco wykorzystano do konsolidacji fazy MAX kompozytów na bazie Ti, Al oraz C. Celem przeprowadzonych badań było wytworzenie zagęszczonych, wolnych od pęknięć kompozytów oraz analiza ich właściwości. Zagęszczone z wykorzystaniem technik udarowych materiały wstępnie wyżarzono w 1173 K w celu usunięcia skutków odkształcenia udarowego. Uzyskany materiał charakteryzował się silnym wiązaniem międzycząsteczkowym, ale zaobserwowano również występowanie mikropęknięć. W syntezowanych i wyżarzonych materiałach, wykorzystaniem techniki dyfrakcji promieni rentgenowskich stwierdzono obecność związków międzymetalicznych typu TiAl, Ti₂Al oraz Ti₃Al, a także ceramik wolnych od tlenków typu TiC oraz Ti₄Al₂C₂. Przy pomocy SEM analizowanorównież warstwową strukturę fazy Ti₄Al₂C₂. Zaobserwowano również, iż współczynnik wydłużenia cieplnego wzrastał wraz ze wzrostem temperatury i obniżał się wraz ze zmniejszaniem się koncentracji TiC.

1. Introduction

Cold explosive shock compaction technique has been applied to consolidate metal, intermetallic, and ceramic powders. However, cracks and pores often generate in the shock compacts [1]. Our research group has offered to utilize simultaneously both the underwater-shock compaction technique and the combustion synthesis as a process to produce various difficult-to-consolidate materials [2,3]. We call it “hot shock compaction”. On the other hand, non-oxide materials and intermetallics are known as some of the promising materials in the fields of lightweight and high temperature functional materials [4-9]. Although various processes for the materials have been developed until now, it was not easy essentially to prepare successful process conditions. To overcome such an inconvenience, it is effective to utilize the combustion synthesis, which can produce various non-oxides and intermetallics. Actually, as one of the examples of execution, our group has

been produced Ti-Al-C system composites by using combustion synthesis [10,11].

In this study, it has been attempted to reveal features of the various Ti-Al-C system non-oxide composites by using the hot shock compaction technique. Especially, properties of the composites annealed at 1173 K were investigated in detail. They were evaluated by taking into consideration X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), Vickers hardness test, and the coefficients of thermal expansion.

2. Experimental procedures**2.1. Sample preparation**

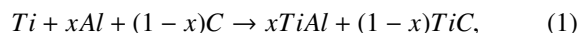
Commercially available powders of titanium (mean particle size: 45 μm, Osaka Titanium Technologies Co., Ltd., Japan), aluminum (17 μm, Toyo aluminum K.K., Japan), and

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graphite (1–2 μm , Sigma-Aldrich Co., USA) were used as raw materials. Ti–Al–C composites were synthesized according to the following reaction,



where, x has a range from 0 to 1.0. Each powder mixture according to the Equation (1) was wet-mixed in ethanol for 1 h, fully dried and then was tapped into the powder container with a cylindrical hole having 20 mm in diameter and 40 mm in height, as shown in Fig. 1. The combustion synthesis was initiated by passing electric current with electric power of 0.6 kVA for 5 s through a tungsten heating coil under atmospheric pressure at room temperature.

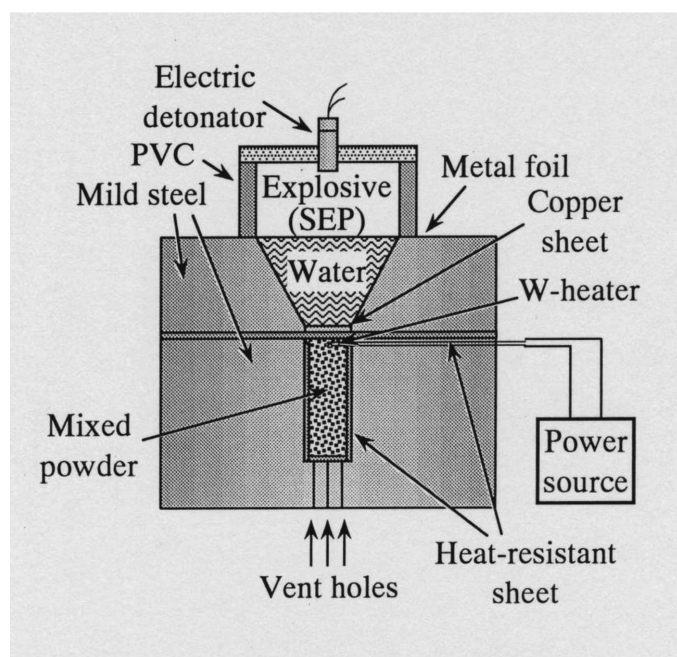


Fig. 1. A schematic illustration of the hot shock compaction assembly

2.2. Measurement of combustion temperature

The maximum temperature during combustion synthesis of powder mixtures in a container were measured prior to explosive compaction test by radiation thermometer which was set above the container with powder mixture. After initiation of combustion synthesis, the temperature was recorded every 0.5 seconds for 1 minute.

2.3. Hot shock compaction and post-annealing

The hot shock compaction assembly consists of explosive, water and powder charged containers (Fig. 1). Plastic explosive “SEP” was used in this experiment. It consists mainly of nitric ester, and is characterized by the detonation velocity of about 6900 m/s. The shock pressure is intensified by reflection of the shock waves on a conical wall of the water container. The estimated magnitude of the shock pressure was about 5 to 10 GPa. The combustion synthesis was initiated with the tungsten heating-coil. It was hypothesized that the powder mixtures would be converted into TiC ceramics and/or TiAl intermetallic compounds after the combustion synthesis

before the explosion. The shock compaction was carried out after 10 to 25 seconds from the initiation of combustion synthesis, depending on their compositions. The obtained shock compacts were subject to post-annealing treatments at 1173 K for 2 hours under vacuum of 10^{-5} torr (1.33×10^{-3} Pa).

2.4. Characterization and observations

The compacted samples were evaluated using the XRD analysis (XRD, RAD-1B, Rigaku Co., Japan), Vickers hardness (load of 4.9 N for 15 sec, NT-M0001, Shimadzu Corp., Japan), and SEM observations (JSM-6301F, JEOL, Japan). The specimens for hardness tests were embedded in the resin and next polished. The properties of thermal expansion were investigated in the temperature region from 473K to 1173K under vacuum of about 10^{-2} torr with the equipment (formastor-F, Fuji Electronic Industrial Co., Ltd, Japan). Prior to the investigation, columnar specimens (3 mm in diameter, 10 mm in length) for the tests were cut off from the shock-compacted composites parallel to the shock wave direction with a wire electrical discharge machine (EDM, DWC-90PF-CNC-7, Mitsubishi Electric Corp., Japan). After that, a hole (2 mm in diameter, 5 mm in depth) for welding the Pt–PtRh thermocouple (\varnothing 0.2 mm) for temperature measurements during the testing was processed on the bottom plane of the columnar specimens with another EDM (DE70-5T, Sankyo Engineering Co. Ltd., Japan). Thin oxide films on the surface of the specimens formed after EDM processing were removed with the diluted hydrochloric acid (0.1 N).

3. Results and discussion

Measurements of maximum temperature during combustion synthesis were listed in TABLE 1. The highest temperature varied from 2405 K to 2009 K with increasing TiAl contents. Unfortunately, we could not get data of maximum temperature for samples with TiC/TiAl = 20/80 and 0/100 because of unstable propagation of combustion wave.

TABLE 1
Maximum temperature during combustion synthesis

Molar ratio (TiC/TiAl)	100/0	80/20	60/40	40/60
Temperature (K)	2405	2260	2176	2009

Outer view of as-synthesized (right) and hot-compacted TiC specimens (left) is shown in Fig. 2. The compacted specimen was compressed into about one fourth in height, in comparison to as-synthesized one. It is clear that hot shock compaction technique could be applied successfully to produce the TiC–TiAl system composite because few macro cracks were found visually in the obtained specimens.



Fig. 2. Outer views of as-synthesized (right) and compacted specimens (left)

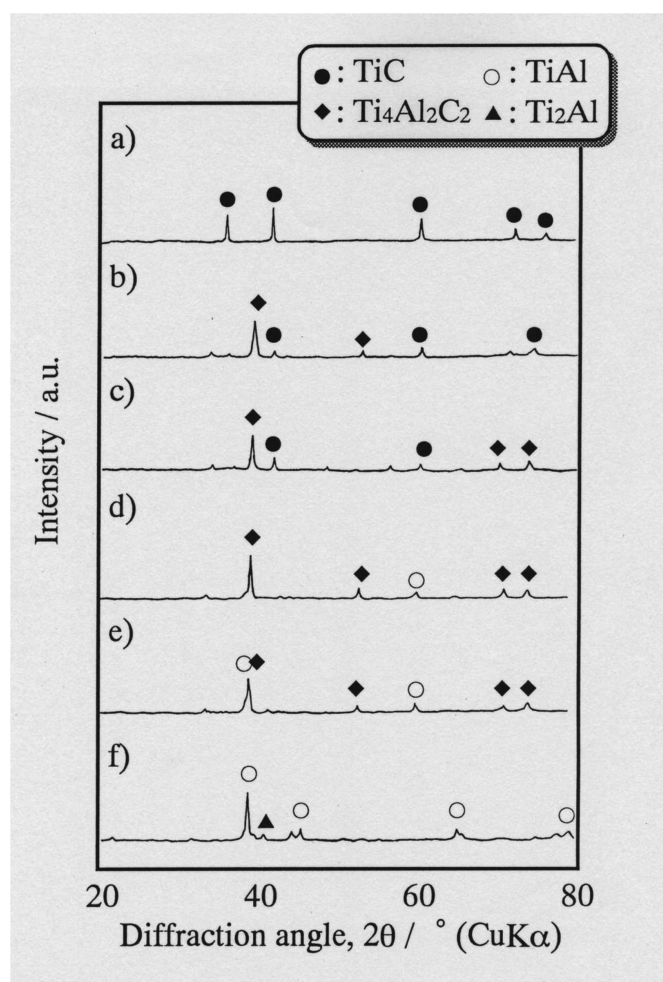


Fig. 3. XRD patterns of specimens annealed at 1173 K for 2 h: (a) TiC/TiAl = 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100

Fig.3 shows the XRD patterns of annealed specimens. They indicated presence of TiC ceramic and TiAl intermetallic compound phases around end members. In addition, $Ti_4Al_2C_2$ phase was detected for samples of the composition TiC: TiAl=80:20 to 20:80. The $Ti_4Al_2C_2$ phase is known as MAX phase, $M_{n+1}AX_n$, where $n = 1, 2, \text{ or } 3$ [10,11]. Here, it should

be noted that XRD patterns were similar extremely to those of as-compacted specimens. This fact suggested that TiC and TiAl phases had caused further reaction to create $Ti_4Al_2C_2$ phase during combustion synthesis prior to shock compaction [12,13].

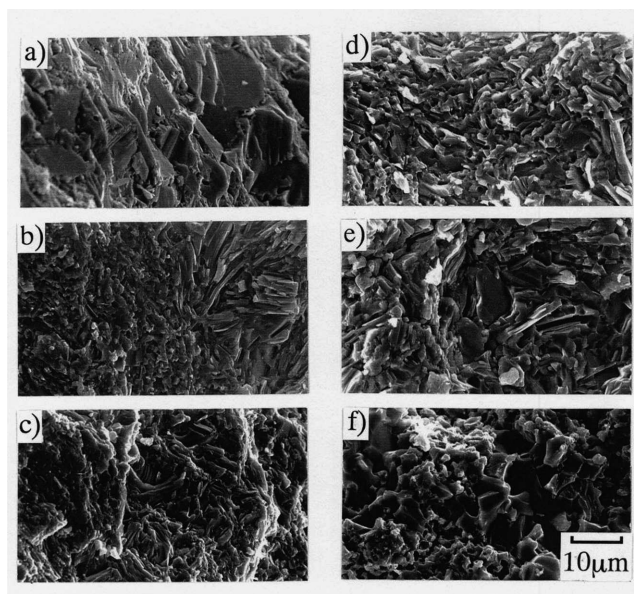


Fig. 4. SEM micrographs of fracture surfaces for various TiAl-C composites annealed at 1173 K: a) TiC/TiAl = 100/0, b) 80/20, c) 60/40, d) 40/60, e) 20/80 and f) 0/100

Fracture surface observations with SEM revealed that the consolidated composites indicated essentially intergranular fracture mode, as shown in Fig. 4. Monolithic TiC specimen exhibited large size crystal grains, whereas TiAl specimen had fine equi-axial crystal grains. Also, the consolidated specimens consisted of crystal grains with the lamella structures except for monolithic TiC and TiAl specimens. TiAl-rich specimens had relatively finer lamella structures, compared with other specimens. This lamella microstructure was one of the characteristic results in this study. The lamella structures are similar to those of Ti_3SiC_2 phase, which is also known as a feature of MAX phase [10]. On the other hand, Y.-L.Chen et al. [14] reported that Ti_2AlC composites were formed after the reaction of TiAl with TiC above $900^\circ C$ [14]. In the present study, it was speculated that the same reaction as their reports would be generated. Also, it was suggested that the specimens had strong bonding strength, because of their high Vickers hardness values what is visual in Fig. 5. Monolithic TiC and TiAl specimens were almost the same hardness values as commercially available materials. In the intermediate compositions, in which $Ti_4Al_2C_2$ phase was produced, their hardness values was between monolithic TiC and TiAl specimens. From these measurements and observations, their presumable strong interparticle bonding must have been given by shock pressure and high temperature during the shock wave processing.

Fig. 6 indicates the measurements results of the coefficients of thermal expansion in the temperature range from 473 K to 1173 K. The monolithic TiAl showed value equals $11.3 \times 10^{-6} / K$ of mean expansion coefficients, whereas TiC-rich composite (TiC- 40 mol% TiAl) had about $9.0 \times 10^{-6} / K$. Also, for samples with compositions of TiC: TiAl = 20:80

and 40:60, in which relatively finer lamella structures were observed, it was found that their expansion coefficients show values between monolithic TiAl and TiC- 40 mol% TiAl specimens. In other specimens, we could not measure the coefficients due to the technical difficulties. Further more, it was obviously comprehended that these two specimens showed similar coefficient of TiC- 40 mol% TiAl at lower temperature, whereas monolithic TiAl at higher temperature. This suggested that specimens with TiAl-rich compositions could be operated flexibly as an engineering material in the wide medium temperature range.

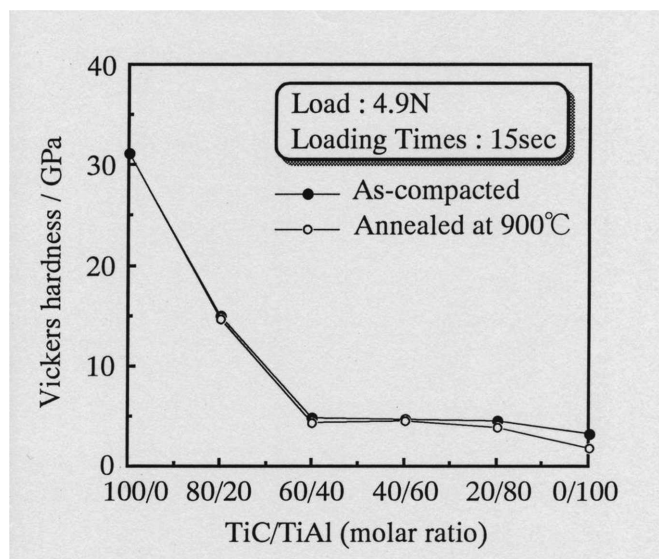


Fig. 5. Variation in Vickers hardness of various Ti-Al-C composites

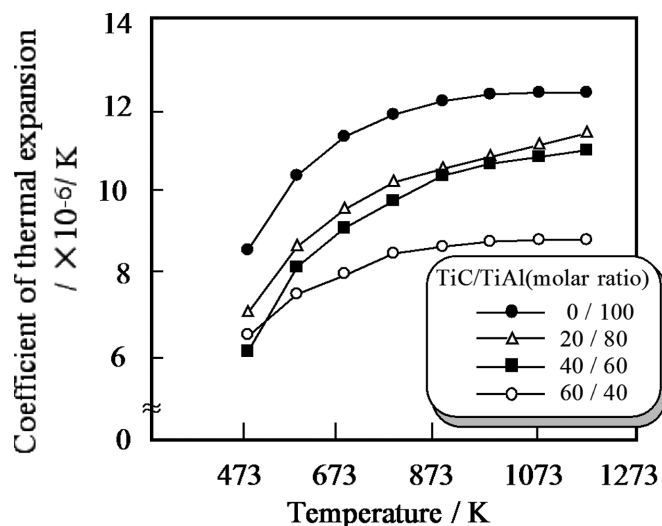


Fig. 6. Relation between temperature and thermal expansion coefficients for various Ti-Al-C composites

4. Conclusions

Various Ti-Al-C composites were produced by hot shock compaction technique, followed by annealing at 1173 K. XRD patterns indicated that the composites were composed of TiC and TiAl phases in the end member compositions of starting materials, whereas $Ti_4Al_2C_2$ phase was also detected in the intermediate compositions. It was speculated that $Ti_4Al_2C_2$ phase had been formed after the reaction of TiAl phase with TiC one during combustion synthesis. The hardness value was lowered as increasing TiAl content up to TiC: TiAl=60:40. In the TiAl-rich composition region, hardness values exhibited almost the same one as those of monolithic TiAl specimen. SEM observations revealed that $Ti_4Al_2C_2$ had lamella structures. On the other hand, monolithic TiAl and TiC consisted of fine equi-axial crystal grains and relatively large grains, respectively. Since the wide variation of thermal expansion coefficient in the medium temperature regions was found, Ti-Al-C system composites can be expected as one of the promising engineering materials.

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