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Formation of $Ti_2AlC_{0.5}N_{0.5}$ solid solutions by combustion synthesis of Al_4C_3-containing samples in nitrogen

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ABSTRACT

Preparation of the solid solution $Ti_2AlC_{0.5}N_{0.5}$ from the powder compacts composed of Ti, Al_4C_3, and Al or AlN was investigated by self-propagating high-temperature synthesis (SHS) under gaseous nitrogen. The molar proportion of three reactant powders was formulated as Ti:Al_4C_3:Al (or AlN) = 2:1/6:1/3. For both types of the samples, the increase of nitrogen pressure from 0.45 to 1.82 MPa augments the combustion temperature and thus accelerates the reaction front. In contrast to the inertness of AlN, Al particles reacted energetically with Ti and N_2 during the SHS process, which resulted in the higher reaction exothermicity for the sample containing Al than that adopting AlN. The solid solution $Ti_2AlC_{0.5}N_{0.5}$ was identified as the dominant phase in the final products from the Ti–Al_4C_3–Al powder compacts. However, the increase of nitrogen pressure adversely affected the evolution of $Ti_2AlC_{0.5}N_{0.5}$, because Ti was over-nitrified and Al also reacted with nitrogen. When AlN was used to replace Al in the reactant compacts, the formation of $Ti_2AlC_{0.5}N_{0.5}$ was deteriorated due to weak exothermicity and deficiency of TiAl. In addition, the products synthesized from the Ti–Al_4C_3–AlN samples under nitrogen of 1.48 and 1.82 MPa were dominated by titanium carbonitride Ti(C,N). This implies that the use of AlN in place of Al is unfavorable for the formation of $Ti_2AlC_{0.5}N_{0.5}$ through combustion synthesis involving gaseous nitrogen.

1. Introduction

Ternary compounds $M_{n+1}AX_n$, 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 either C or N, are a class of materials with a unique combination of metallic and ceramic properties [1–3]. In general, the MAX phases are relatively soft, readily machinable, good thermal and electrical conductors, elastically stiff, and highly resistant to thermal shock, oxidation, and corrosion [1–3]. Extensive studies were performed on many MAX compounds, such as Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC, Cr_2AlC, and Ti_2AlN [4–10]. Fabrication of the MAX phases has been conducted through a variety of processing routes; for example, hot pressing (HP) [2,4,5], hot isostatic pressing (HIP) [6,7], in situ hot pressing/solid–liquid reaction synthesis [10–15], pulse discharge sintering (PDS) [16–19], and self-propagating high-temperature synthesis (SHS) [20–25].

Furthermore, solid solutions based on the MAX phases can be formed on either the M, A, or X site, which renders great potential for tailoring and/or optimizing the material properties. Various MAX-based solid solutions, like $(Ti,Nb)_2AlC$, $(Cr,V)_2AlC$, $(Cr,V)_2GeC$, $Ti_3(Si,Al)C_2$, $Ti_3(Si,Ge)C_2$, and $Ti_2Al(C,N)$, were prepared and their mechanical and thermal properties were studied [26–35]. Of particular interest for this work is $Ti_2AlC_{0.5}N_{0.5}$, which possesses enhanced properties when compared with two related end members Ti_2AlC and Ti_2AlN [7,32–34]. According to Barsoum and co-workers [7,32–35], $Ti_2Al(C,N)$ was produced from the stoichiometric mixtures of Ti, Al_4C_3 or Al, AlN, and graphite powders by hot isostatic pressing at 1300–1400 °C and 40–100 MPa for 10–15 h.

As a promising alternative, combustion synthesis in the SHS mode takes advantage of the self-sustaining merit from highly exothermic reactions, and hence, has the benefits of low energy requirement, short reaction time, and simple facilities [36–39]. The SHS technique has been effectively utilized to produce a number of the MAX carbides, like Ti_3SiC_2 [20], Ti_3AlC_2 [21], Ti_2AlC [22], Ta_2AlC [23], Nb_2AlC [24], and Ti_2SnC [25]. Recently, Yeh et al. [40] first prepared $Ti_2AlC_{0.5}N_{0.5}$ from TiC- and TiN-diluted Ti–Al–C powder compacts by combustion synthesis in either solid–gas or solid state mode. Formation of $Ti_2AlC_{0.5}N_{0.5}$ with three minor phases TiC, TiN, and Ti_3Al was achieved by solid–gas combustion of the TiC-diluted samples in nitrogen [40]. For the TiN-added samples, the SHS process executed in the solid state was beneficial to reduce the secondary phases, which yielded $Ti_2AlC_{0.5}N_{0.5}$ with trivial amounts of TiC and TiN [40].

As an extension of the previous effort [40], this study makes the first attempt to employ Al_4C_3-containing powder compacts for the preparation of $Ti_2AlC_{0.5}N_{0.5}$ through the SHS process under gaseous

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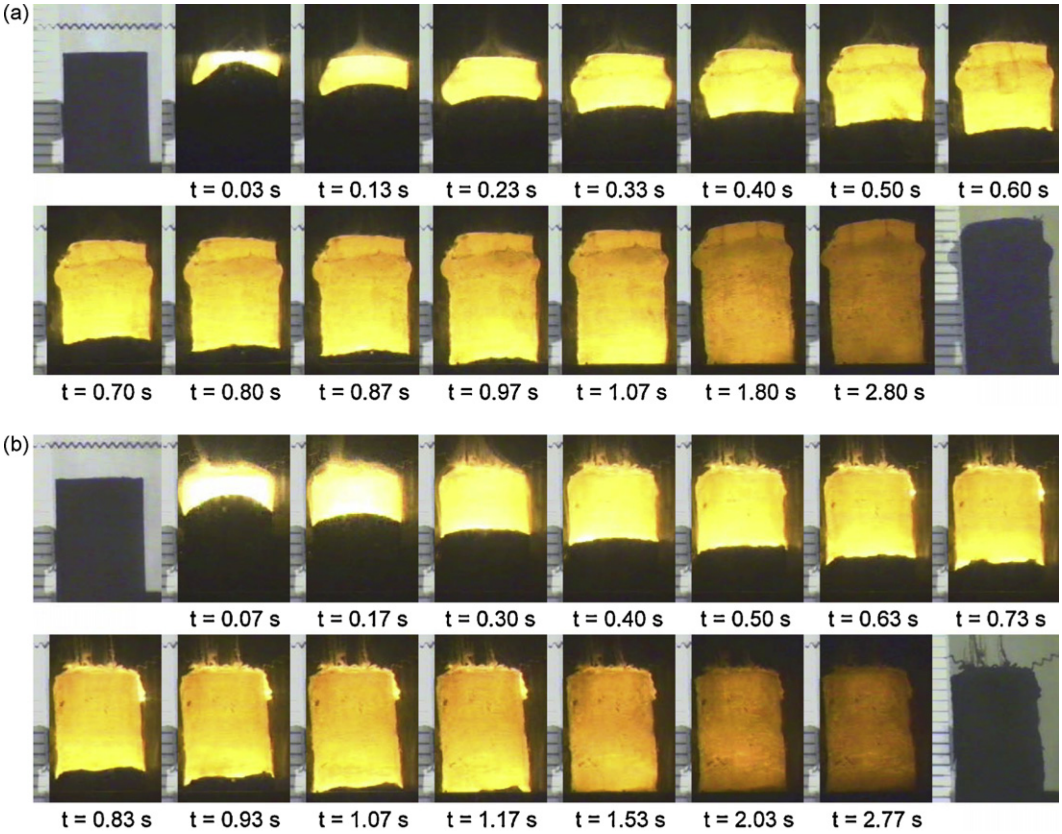

Fig. 1. Typical SHS sequences in nitrogen of 0.45 MPa associated with powder compacts of different initial compositions: (a) $2Ti + 1/6Al_4C_3 + 1/3Al$ and (b) $2Ti + 1/6Al_4C_3 + 1/3AlN$.

nitrogen. Effects of the sample stoichiometry and nitrogen pressure are investigated on the phase composition of the final product, as well as on the combustion temperature and propagation velocity of the reaction front. Moreover, the reaction mechanism describing the formation of $Ti_2AlC_{0.5}N_{0.5}$ from the Ti–Al_4C_3–Al sample in nitrogen is proposed on the basis of the phase composition of the final product.

2. Experimental methods of approach

The starting materials adopted in this study are inspired by those (Ti, Al, Al_4C_3, AlN, and carbon) used by Barsoum and co-workers [7,32–35] in the process of hot isostatic pressing. In order to assure self-sustaining combustion in nitrogen, this work employs two types of the Al_4C_3-containing samples. One is composed of titanium (Strem Chemicals, ≤45 μm, 99% purity), aluminum (Showa Chemical Co., ≤40 μm, 99% purity), and Al_4C_3 (Strem Chemicals, ≤45 μm, 98% purity) at a molar proportion of Ti:Al_4C_3:Al = 2:1/6:1/3. The other replaces elemental aluminum with AlN (Strem Chemicals, 2.5–4.0 μm, 99% purity) to form an initial stoichiometry of Ti:Al_4C_3:AlN = 2:1/6:1/3. The reactant powders were well mixed in a ball mill and then cold-pressed into cylindrical compacts with a diameter of 7 mm, a height of 12 mm, and a compaction density of 55% relative to the theoretical maximum density (TMD).

The SHS experiments were conducted in a stainless-steel windowed chamber filled with high-purity nitrogen (99.999%) from 0.45 to 1.82 MPa. Details of the experimental setup and measurement approach were reported elsewhere [41,42]. The microstructure of synthesized products was examined under a scanning electron microscope (Hitachi S-3000N), and the phase composition was analyzed by an X-ray diffractometer (Shimadzu XRD-6000) with CuK_α radiation.

3. Results and discussion

3.1. Observation of combustion characteristics

Fig. 1(a) and (b) illustrates typical SHS images recorded from combustion of two different types of powder compacts in nitrogen of 0.45 MPa. It is evident that upon ignition a distinct reaction front forms and propagates downward in a self-sustaining manner, which transforms the cold reactant into an incandescent combustion product. Because nitrogen is normally insufficient within the sample compact for combustion synthesis involving gaseous reagent, continuous infiltration of nitrogen proceeds after the passage of the combustion wave, which leads to subsequent nitridation and prolonged combustion luminosity. As indicated in Fig. 1(a) and (b), a shorter propagation period of the combustion wave is noticed for the Ti–Al_4C_3–Al powder compact than the Ti–Al_4C_3–AlN sample. This is most likely due to the fact that combustion of the sample adopting Al is more exothermic than that of the AlN-containing sample.

3.2. Measurement of flame-front propagation velocity and combustion temperature

Fig. 2 presents the influence of nitrogen pressure on the propagation velocity of the combustion front (V_f). The combustion velocity increases with increasing pressure of nitrogen for both types of the samples, on account of a higher concentration of nitrogen in the reaction front. As mentioned above, the use of AlN instead of Al in the reactant compact lowers the flame-front velocity, because AlN is essentially inert during the SHS process. On the contrary, Al reacts with nitrogen and Ti to form nitrides and aluminides, respectively, and both reaction paths are exothermic. Therefore, the higher overall reaction exothermicity is anticipated for the Ti–Al_4C_3–Al sample, which thereby accelerates the combustion wave.

Three temperature profiles recorded from combustion of the Ti–Al_4C_3–Al samples under nitrogen of different pressures are depicted in Fig. 3. The abrupt rise in temperature signifies the rapid arrival of the combustion wave. The peak value corresponds

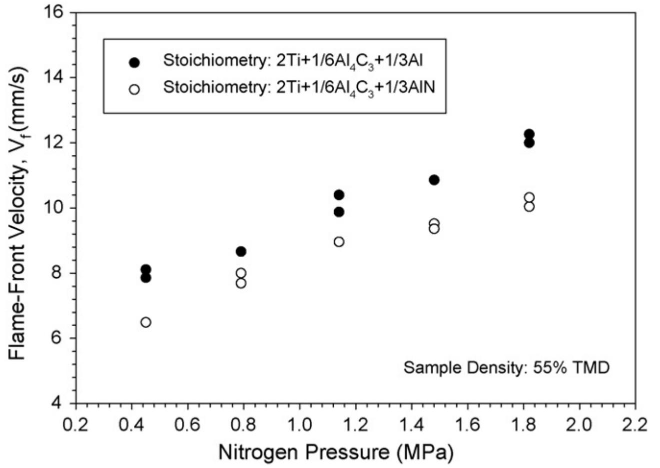

Fig. 2. Effects of nitrogen pressure and sample stoichiometry on flame-front propagation velocity of two types of Al_4C_3-added powder compacts.

to the flame-front temperature. In agreement with the pressure dependence of the combustion velocity, the reaction front temperature of the Ti–Al_4C_3–Al sample increases from 1532 to 1755 °C with increasing nitrogen pressure from 0.45 to 1.82 MPa. For the Ti–Al_4C_3–AlN powder compacts, Fig. 4 reveals a similar variation of combustion temperature with nitrogen pressure to that shown in Fig. 3, except for the lower peak temperatures ranging between 1410 and 1632 °C. This confirms a decline in the reaction exothermicity for the reactant compact adopting AlN in place of Al.

3.3. Composition and morphology analysis of combustion products

Typical XRD patterns of the final products obtained from combustion of the Ti–Al_4C_3–Al powder compacts in nitrogen of different pressures are presented in Fig. 5(a)–(c), within which $Ti_2AlC_{0.5}N_{0.5}$ is identified as the dominant phase. In addition to $Ti_2AlC_{0.5}N_{0.5}$, the final products contain secondary components which vary essentially with nitrogen pressure. Fig. 5(a) indicates three minor phases, TiN, TiC, and Ti_3Al, in the product synthesized at 0.45 MPa of nitrogen. As the pressure of nitrogen increases, Fig. 5(b) and (c) shows the increase of TiC and TiN and the presence of AlN. Based upon the thermodynamic consideration, it is believed that the formation of $Ti_2AlC_{0.5}N_{0.5}$ is initiated by the reaction of Ti with nitrogen, as follows:

$$2Ti + N_2 \rightarrow 2TiN \tag{1}$$

With the high reaction heat ($\Delta H_{f,TiN} = -337.7$ kJ/mol) liberated from Reaction (1), the reaction of Ti with Al was triggered and the intermetallic compounds Ti_3Al and TiAl were formed according to Reactions (2) and (3), respectively.

$$3Ti + Al \rightarrow Ti_3Al \tag{2}$$

$$Ti_3Al + 2Al \rightarrow 3TiAl \tag{3}$$

Titanium aluminide TiAl is recognized as an important intermediate in the evolution of Ti_2AlC and Ti_2AlN [43,15], from both of which the solid solution $Ti_2AlC_{0.5}N_{0.5}$ is produced. During the SHS process of this study, TiAl is also generated from the reaction between Ti and Al_4C_3. The above reaction sequences are expressed in the following:

$$7Ti + Al_4C_3 \rightarrow 4TiAl + 3TiC \tag{4}$$

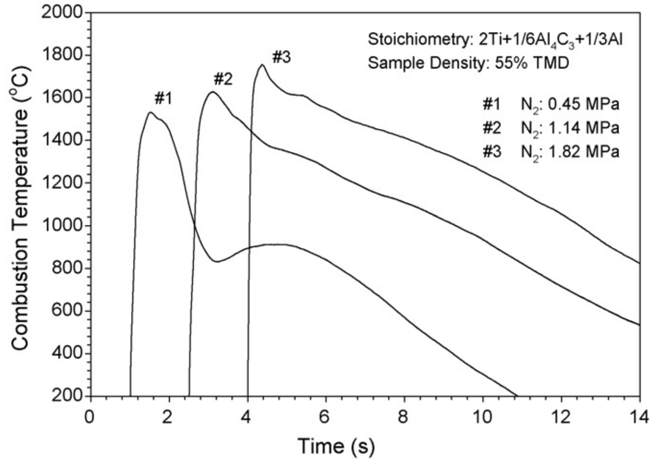

Fig. 3. Effect of nitrogen pressure on combustion temperature associated with powder compacts composed of $2Ti + 1/6Al_4C_3 + 1/3Al$.

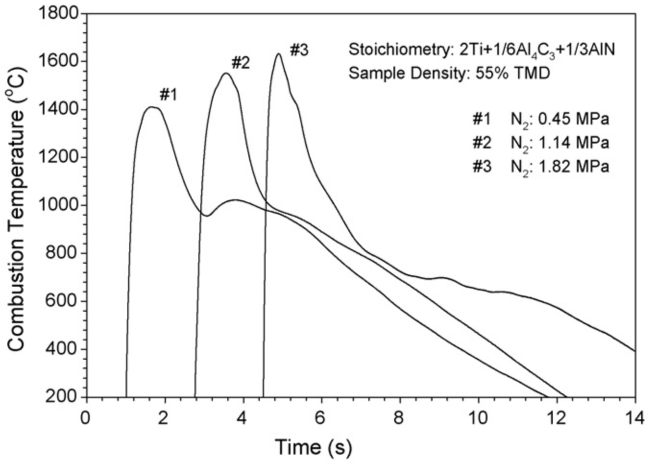

Fig. 4. Effect of nitrogen pressure on combustion temperature associated with powder compacts composed of $2Ti + 1/6Al_4C_3 + 1/3AlN$.

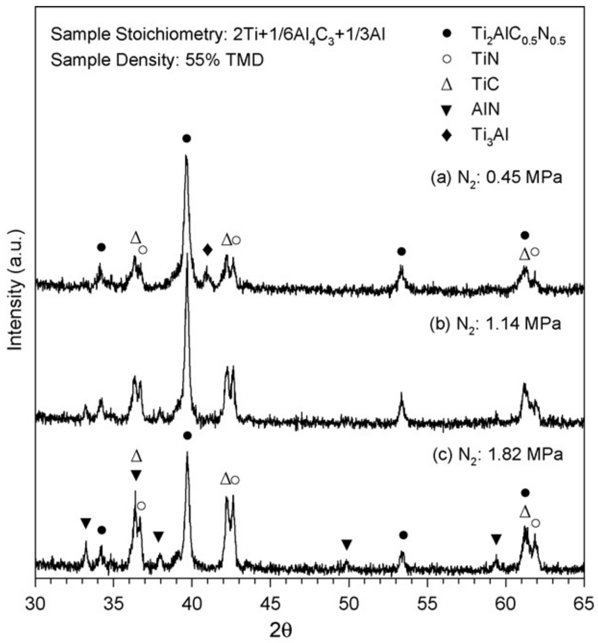

Fig. 5. XRD patterns of products synthesized from powder compacts of $2Ti + 1/6Al_4C_3 + 1/3Al$ in nitrogen of (a) 0.45 MPa, (b) 1.14 MPa, and (c) 1.82 MPa.

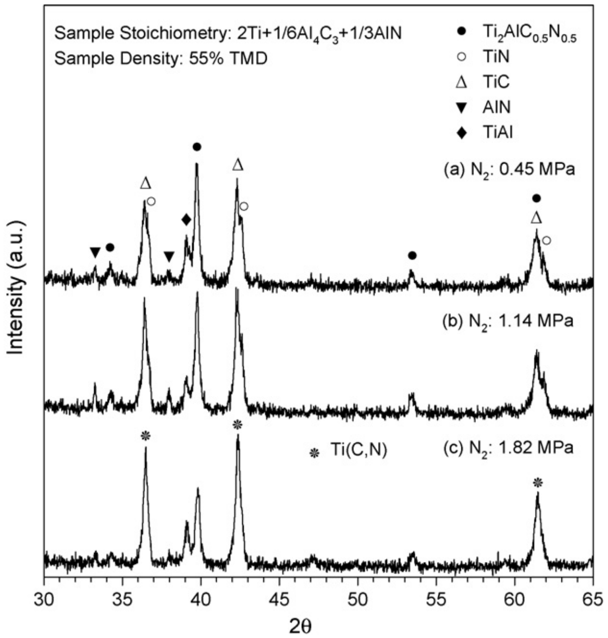

Fig. 6. XRD patterns of products synthesized from powder compacts of $2Ti + 1/6Al_4C_3 + 1/3AlN$ in nitrogen of (a) 0.45 MPa, (b) 1.14 MPa, and (c) 1.82 MPa.

$$TiAl + TiC \rightarrow Ti_2AlC \quad (5)$$

$$TiAl + TiN \rightarrow Ti_2AlN \quad (6)$$

$$Ti_2AlC + Ti_2AlN \rightarrow 2Ti_2AlC_{0.5}N_{0.5} \quad (7)$$

The presence of AlN in Fig. 5(b) and (c) means that Al reacts not only with Ti but also with nitrogen when the pressure of nitrogen increases. The increase of nitrogen pressure also causes excessive nitridation of Ti. Consequently, the formation of $Ti_2AlC_{0.5}N_{0.5}$ is deteriorated by increasing the nitrogen pressure, as shown in Fig. 5(b) and (c).

For the $Ti–Al_4C_3–AlN$ powder compacts combusting in nitrogen, although Fig. 6(a)–(c) indicates that the final products are composed of $Ti_2AlC_{0.5}N_{0.5}$, TiAl, TiN, TiC, and AlN, the evolution of $Ti_2AlC_{0.5}N_{0.5}$ is inferior to that presented in Fig. 5. Due to the lack of Al in the samples to react with Ti, Fig. 6(a)–(c) shows high contents of TiN resulting from excessive nitridation. Moreover, the incomplete phase conversion led to a considerable amount of TiC left in the final products. With the increase of nitrogen pressure, TiN and TiC tends to form another solid solution, titanium carbonitride Ti(C,N) [44]. As revealed in Fig. 6(c), the product synthesized in nitrogen of 1.82 MPa is dominated by Ti(C,N). This suggests that the use of AlN instead of Al in the Al_4C_3-containing sample is unfavorable for the formation of $Ti_2AlC_{0.5}N_{0.5}$ by combustion synthesis under nitrogen.

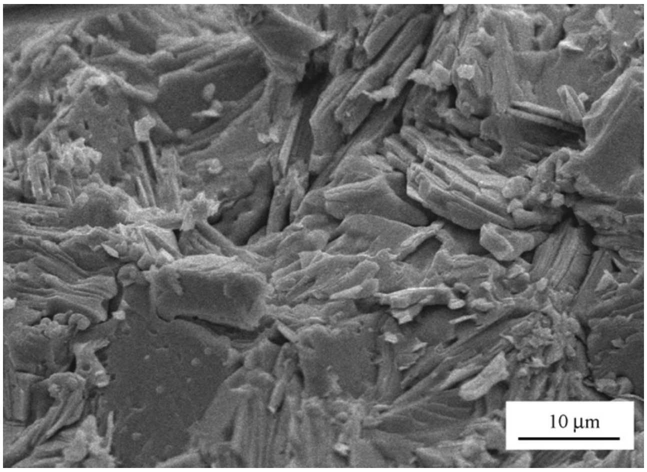

Fig. 7. SEM micrograph illustrating fracture surface of the product synthesized from a powder compact of $2Ti + 1/6Al_4C_3 + 1/3Al$ in nitrogen of 0.45 MPa.

The SEM micrograph illustrating the typical fracture surface of the synthesized product is presented in Fig. 7, within which plate-like $Ti_2AlC_{0.5}N_{0.5}$ grains are closely stacked. The $Ti_2AlC_{0.5}N_{0.5}$ grain has a size of about 8–12 μm and a thickness of 1–2 μm. Such a laminated structure is characteristic of the ternary MAX compound.

4. Conclusions

Preparation of the solid solution $Ti_2AlC_{0.5}N_{0.5}$ from Al_4C_3-containing powder compacts was conducted by the SHS process under nitrogen of 0.45–1.82 MPa. In addition to Al_4C_3, the green samples consisted of Ti and Al or AlN and were formulated with a molar proportion of $Ti:Al_4C_3:Al$ (or AlN) = 2:1/6:1/3.

On account of the higher nitrogen concentration, the flame-front temperature increased with increasing nitrogen pressure for both types of the reactant compacts. Moreover, the variation of the reaction front velocity with nitrogen pressure was found to be in a manner consistent with that of combustion temperature. Because of the inertness of AlN during the SHS process, the use of AlN instead of Al in the reactant mixture reduced the overall reaction exothermicity, which is responsible for the lower reaction temperature and slower combustion wave observed in the sample of $Ti–Al_4C_3–AlN$.

For the $Ti–Al_4C_3–Al$ powder compacts, the solid solution $Ti_2AlC_{0.5}N_{0.5}$ was identified as the dominant constituent in the final products and better yield of $Ti_2AlC_{0.5}N_{0.5}$ was achieved under nitrogen of lower pressures. Depending upon the nitrogen pressure, various secondary phases, such as TiC, TiN, Ti_3Al, and AlN, were detected. As the pressure of nitrogen increased up to 1.14 MPa and above, the nitridation of Al and Ti surpassed the reaction between Al and Ti, which in turn diminished the evolution of $Ti_2AlC_{0.5}N_{0.5}$.

For the $Ti–Al_4C_3–AlN$ samples, the final products were composed of $Ti_2AlC_{0.5}N_{0.5}$, TiAl, TiN, TiC, and AlN, but the degree of $Ti_2AlC_{0.5}N_{0.5}$ formation was inferior to that associated with the $Ti–Al_4C_3–Al$ powder compacts. Moreover, the content of $Ti_2AlC_{0.5}N_{0.5}$ decreased substantially with increasing nitrogen pressure. It was found that the products synthesized in nitrogen of 1.48 and 1.82 MPa were dominated by titanium carbonitride Ti(C,N).

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