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Synthesis and mechanical properties of Ti_3AlC_2 by hot pressing TiC_x/Al powder mixture

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Abstract

A study has been performed to synthesize polycrystalline bulk Ti_3AlC_2 by hot pressing from TiC_x ($x = 0.6$) and Al powder mixture at the temperature range of 800–1600 °C under 25 MPa for various times. Relatively pure Ti_3AlC_2 was successfully synthesized above 900 °C. Small amount of Ti_2AlC as a secondary phase was observed along with Ti_3AlC_2 below 1400 °C. With increasing hot pressing time to 1250 °C, the amount of un-reacted TiC_x was gradually decreased while Ti_3AlC_2 was appeared to be a dominant phase. The densification of Ti_3AlC_2 was examined as a function of hot pressing temperature up to 1600 °C as well as it was investigated with hot pressing time at 1250 °C. Near fully dense Ti_3AlC_2 was synthesized as the hot pressing time was increased at 1250 °C. Fully dense and pure Ti_3AlC_2 could be synthesized by hot pressing above 1400 °C. The resulting Ti_3AlC_2 above 1400 °C showed the typical laminated and platelet grain structure of ternary carbides. With increasing processing temperature to 1600 °C, the typical platelet grain structure of Ti_3AlC_2 was started to be destroyed and significant grain coarsening was occurred, which might be caused by partial melting of Ti_3AlC_2. The Vickers hardness of bulk Ti_3AlC_2 was about 3.5–6 GPa under the loading of 10 N. The maximum flexural strength of synthesized bulk Ti_3AlC_2 was over 900 MPa. The new process using TiC_x/Al powder mixture as a starting material made it possible to shorten the synthesis time, to reduce processing temperature, as well as to improve the flexural strength of Ti_3AlC_2.

Keywords: Ti_3AlC_2; Synthesis; Ternary carbide; Mechanical properties

1. Introduction

The ternary carbides and nitrides with layered structure have been given attention since they possess many of good properties both of metals and ceramics. The layered ternary carbides and nitrides are chemical resistant, heat resistant and maintain strength at high temperatures. Surprisingly, they are readily machinable, relatively soft compare to transition metal carbides and nitrides, good electrical and thermal conductors, damage tolerant, and thermal shock resistant.[1–5]

Most of previous studies on ternary carbides have been concentrated on Ti_3SiC_2, but not many for Ti_3AlC_2 due to difficulties in synthesis of bulk Ti_3AlC_2 with high purity. One of the ternary carbide '312' families, Ti_3AlC_2, was first synthesized by Pietzka and Schuster in the system of Ti, TiAl, Al_4C_3, and carbon powder mixture in 1994.[6] Ti_3AlC_2 was found to be isostructure with Ti_3SiC_2 and it belongs to a hexagonal crystalline system with lattice parameters of a and c as 0.30753 nm and 1.8578 nm, respectively.[2,3,7]

A few powder metallurgical processes have been reported to fabricate a bulk high purity Ti_3AlC_2. Barsoum et al. fabricated bulk Ti_3AlC_2 by hot isostatic pressing (HIP) at 1400 °C for 16 h under 70 MPa using a powder mixture of Ti, Al_4C_3, and graphite powders.[1] In their study, the Vickers hardness, the Young's modulus, the flexural strength, and the compressive strength of synthesized bulk Ti_3AlC_2 were reported as 4 GPa, 333 GPa, 560 MPa, and 375 MPa, respectively.[1] However, it requires long processing time, high pressure, and high temperature. In their process, Al_4C_3 was used to avoid Al loss by evaporation during the synthesizing process, but it was reported that about 4 vol.% of secondary phases (mostly Al_2O_3) was presented in the synthesized bulk Ti_3AlC_2 by hot isostatic pressing due to the reaction between Al_4C_3 and H_2O. Chen and Zhou[8] also studied to synthesize Ti_3AlC_2 at 1500 °C under 25 MPa by hot pressing using a mixture of Ti, Al, and graphite with various contents of α-Al_2O_3. The Vickers hardness, the flexural strength, and the fracture toughness of synthesized bulk Ti_3AlC_2 with 5 vol.%

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Al_2O_3 were about 3.8 GPa, 420 MPa, and 8.5 MPa $m^{1/2}$, respectively. Zhou et al.[9] and Ge and Chen[10] reported that Ti_3AlC_2 was synthesized by self-propagating high temperature synthesis (SHS) method using Ti, Al, and carbon black powder mixture. It is interesting that they synthesized relatively pure Ti_3AlC_2 with small amounts of TiC and Ti_2AlC as secondary phases by SHS process although elemental Al, Ti, and carbon black were used in starting powder mixture. Wang and Zhou[11] also fabricated a fully dense and relatively pure Ti_3AlC_2 by a solid–liquid reaction and simultaneous in situ hot pressing using Ti, Al, and graphite powder mixture at 1500 °C in only for 5 min. However, they found secondary phases such as TiC, Ti_2AlC, and graphite in the bulk Ti_3AlC_2 fabricated below 1500 °C, which might be due to the complicated reaction paths in the reaction system consisting of Ti, Al, and carbon elemental powders. The flexural strength, the fracture toughness, and Vickers hardness of the Ti_3AlC by Wang and Zhou were about 340 MPa, 7.2 MPa $m^{1/2}$, and 2.5–4.7 GPa, respectively.[11] Recently, Zhou et al.[12] reported that spark plasma sintering (SPS) method is an economical and simple way to fabricate fully dense Ti_3AlC_2 with relatively high purity from either: (1) Ti, Al, and activated carbon powder mixture or (2) Ti, Al_4C_3, and activated carbon powder mixture. It was also reported that excess Ti and Al should be added to compensate the loss of Ti and Al by evaporation during SPS process.

In the present study, we developed a fabrication process for synthesizing bulk Ti_3AlC_2 with high purity using new starting materials to eliminate or minimize the formation of intermediate phases during the synthesis process. Polycrystalline bulk Ti_3AlC_2 was synthesized by hot pressing using TiC_x ($x = 0.6$) and Al powder mixture as a staring material which might make it possible to shorten the synthesis time, to reduce processing temperature, as well as to increase the purity for Ti_3AlC_2. We examined the effects of hot pressing temperature and time on microstructure, densification, and mechanical properties of synthesized Ti_3AlC_2 and also discussed the role of starting materials used in this study for synthesis as well as mechanical properties of Ti_3AlC_2.

2. Experimental procedures

Pure Al and TiC_x ($x = 0.60$) mixed powders were used as starting materials for fabrication of bulk Ti_3AlC_2. TiC_x ($x = 0.6$) was synthesized by a high temperature reaction using Ti powder (<45 μm, 99.9% purity, High purity chemicals, Japan) and graphite powder (average particle size 10 μm, 99.95% purity, SEC Corp.) mixture with a following process: Ti and graphite powder were mixed with a composition of Ti:C = 3:1.8 in molar ratio using SPEX^{TM} mill (8000M Mixer/Mill, Spexmill Inc.) for 30 min in Ar; and then formed into a cylindrical shaped green body by a uni-axial pressing at 20 MPa followed by a cold isostatic pressing at 40 MPa. Ti/graphite green body was heat treated under the vacuum of 1×10^{-2} Torr at 1550 °C for 3 h which formed a bulk TiC_x. The synthesized TiC_x was ground in Ar and then screened TiC_x powders sized under 45 μm.

The synthesized TiC_x and commercially available Al powder (<45 μm, 99.7% purity, Strem chemicals Inc.) were then mixed 3–1.1 in molar ratio using SPEX^{TM} mill in Ar for 10 min. The TiC_x/Al powder mixture was put into the BN spray coated graphite mold. Finally, bulk Ti_3AlC_2 was synthesized by hot pressing at the temperature range of 800–1600 °C under 25 MPa for 0–4 h in Ar.

X-ray diffraction (M03XHF^{22}, MAC Science Co. Ltd.) studies were performed to confirm crystalline phases of the synthesized Ti_3AlC_2. The density of synthesized bulk Ti_3AlC_2 was measured by Archimedes method. The microstructure of the bulk Ti_3AlC_2 was examined by scanning electron microscope (XL-30 FEG, FEI) equipped with energy dispersive spectroscopy (EDS) after polishing and etching with a $HF–HNO_3–H_2O$ solution the synthesized bulk Ti_3AlC_2 specimen. Furthermore, a study of high resolution transmission electron microscopy (JEM 4010, Jeol) has been performed with Ti_3AlC_2 synthesized by hot pressing at 1250 °C and 1400 °C. Three point bending tests (3360 series, Instron Corp.) were performed to measure flexural strength of bulk Ti_3AlC_2 specimen with dimensions of 3 mm × 4 mm × 25 mm, for which span size and cross head speed used were 20 mm and 0.5 mm/min, respectively. Vickers hardness test (Micro Photonics Inc.) was performed on the fine polished surface of bulk Ti_3AlC_2 by varying indentation load between 10 N and 100 N.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of bulk Ti_3AlC_2 specimen synthesized by a hot pressing method using TiC_x ($x = 0.6$) and Al mixed powder as a starting materials at the temperature range of 800–1600 °C for 60 min under 25 MPa. As shown in Fig. 1(a), for the specimen synthesized at 800 °C, un-reacted TiC_x and Al were found to be main crystalline phases, and Ti_2AlC was presented as a minor phase. As the hot pressing temperature was increased to 1000 °C, Ti_3AlC_2 with small amount of Ti_2AlC was to be a main crystalline phase and some of un-reacted TiC_x was remained as a miner phase. With further increasing the hot pressing temperature, the contents of un-reacted TiC_x and Ti_2AlC second phases were

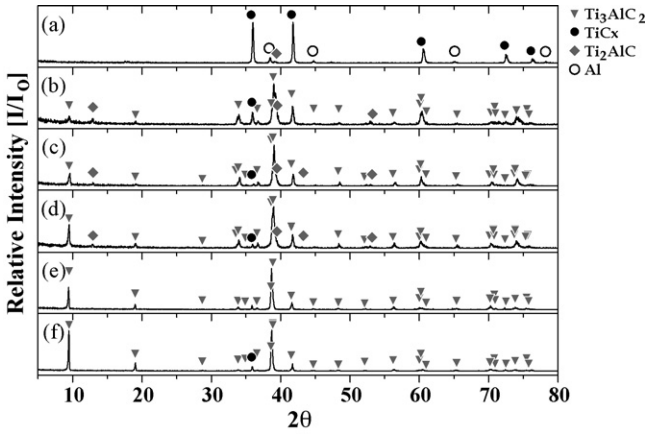

Fig. 1. XRD patterns of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at various temperatures of (a) 800 °C, (b) 1000 °C, (c) 1250 °C, (d) 1300 °C, (e) 1500 °C, and (f) 1600 °C for 60 min under 25 MPa.

gradually decreased while the intensity of Ti_3AlC_2 peaks are getting stronger with hot pressing temperature. For the specimen synthesized at 1400 °C and 1500 °C shown in Fig. 1(d) and (e), most of all phases were identified as Ti_3AlC_2. However, as shown in Fig. 1(f), small amounts of TiC_x was appeared in the specimen synthesized at 1600 °C, which might be due to the partial decomposition of synthesized Ti_3AlC_2 at 1600 °C.

Fig. 2 shows SEM microstructures of Ti_3AlC_2 specimen synthesized by a hot pressing method at the temperature range of 800–1600 °C for 60 min under 25 MPa. Fig. 2(a) shows SEM microstructures of fracture surface for the specimen synthesized at 800 °C. Un-reacted TiC_x particles covered with un-reacted Al were found; presumably Al remained at the surface of TiC_x particles at this temperature. The microstructure of etched surface of Ti_3AlC_2 synthesized at 1000 °C is shown in Fig. 2(b). Striped etching patterns with a certain direction were observed inside of synthesized Ti_3AlC_2 particles that the shape was not different from those of starting TiC_x particles. As can be seen in Fig. 2(c), plate-like structures are visible as well as relatively dense bulk Ti_3AlC_2 was synthesized with increasing the hot pressing temperature. Platelet shaped Ti_3AlC_2 grains became apparent in the microstructures of specimens synthesized at 1400 °C with aspect ratio of platelet developed as high as five (see Fig. 2(d)). With further increase of the hot pressing temperature, the grain size of Ti_3AlC_2 was increased, but the aspect ratio of Ti_3AlC_2 grains was preserved as shown in Fig. 2(e). It was also observed that each platelet shaped Ti_3AlC_2 grains were consisting of laminated layers which has been reported in previous studies.[1–3,7–14] When the hot pressing temperature reached to 1600 °C, Ti_3AlC_2 grain was unexpectedly grown as shown in Fig. 2(f). And, the shape of Ti_3AlC_2 grain was significantly changed by partial loosing platelet grain structure and the aspect ratio of Ti_3AlC_2 grain was decreased to about 1.5–2.0. These sudden changes in microstructures of Ti_3AlC_2 at 1600 °C might be due to

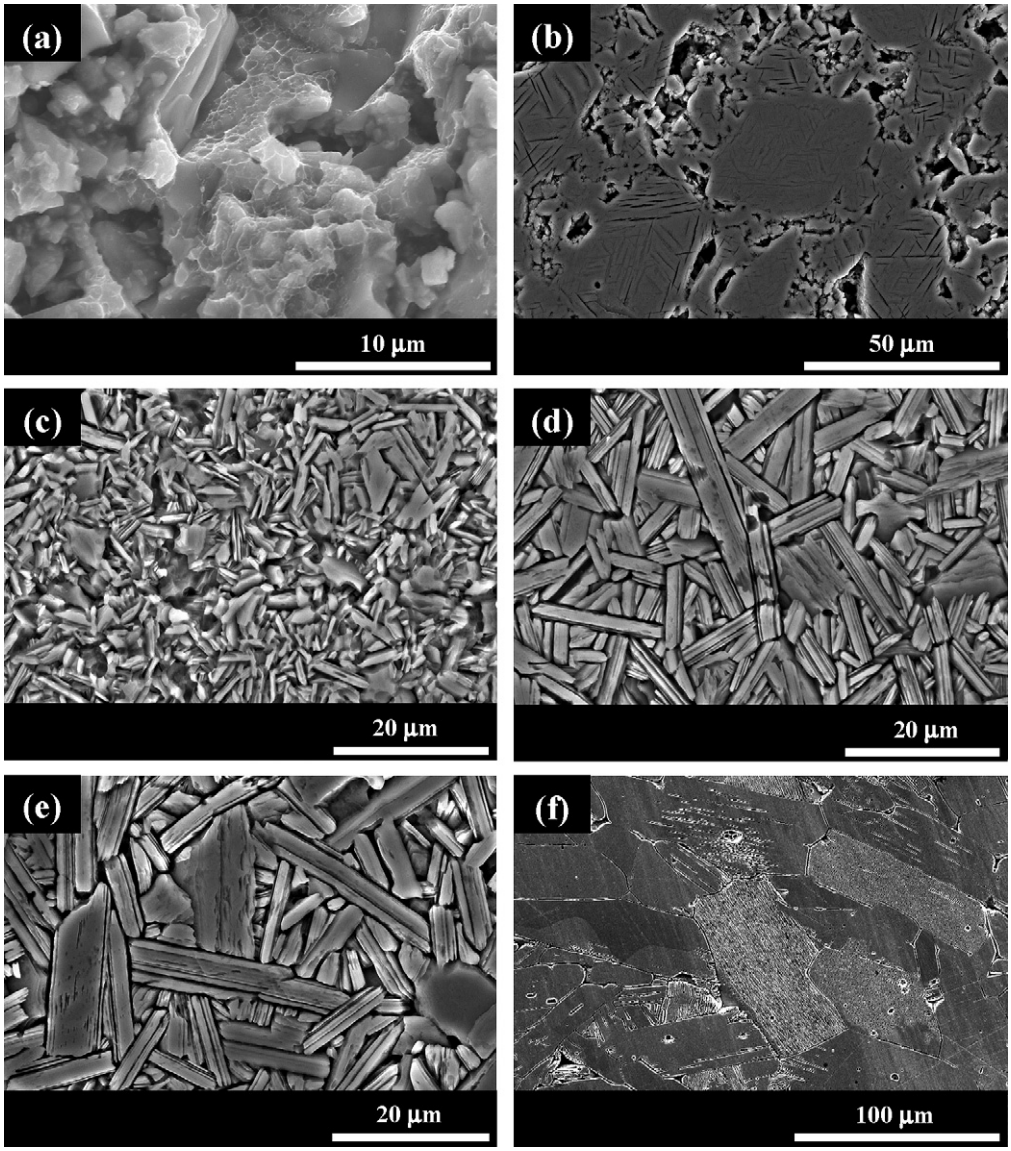

Fig. 2. SEM micrographs of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at various temperatures of (a) 800 °C, (b) 1000 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, and (f) 1600 °C for 60 min under 25 MPa.

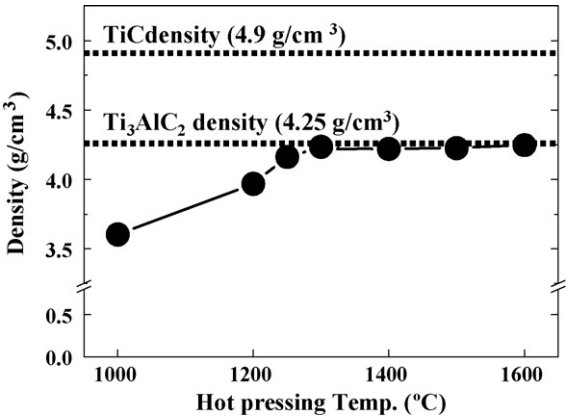

Fig. 3. Density change of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at various temperatures of 800–1600 °C for 60 min under 25 MPa.

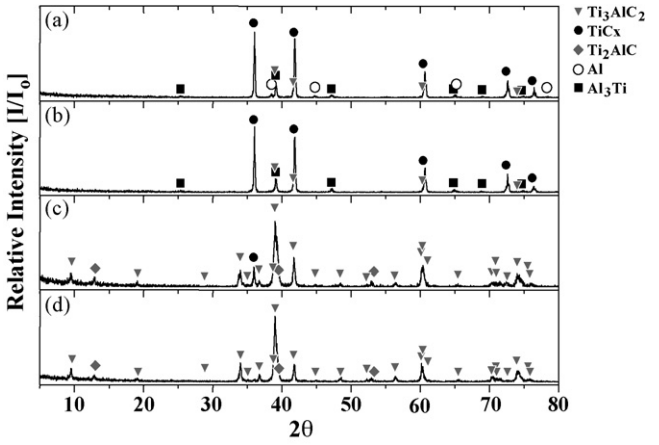

Fig. 4. XRD patterns of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at 1000 °C with various reaction time for (a) 0 min, (b) 10 min, (c) 60 min, and (d) 240 min under 25 MPa.

either partial melting of Ti_3AlC_2 or partial decomposition of Ti_3AlC_2. The partial melting of Ti_3AlC_2 would be a main reason for this drastic change in microstructures of Ti_3AlC_2 because the curved grain boundaries of Ti_3AlC_2 grains are observed in Fig. 2(f), which presumably was occurred by rapid grain boundary migrations and grain growth due to partial melting of Ti_3AlC_2 grains. Moreover, it was clearly observed that melt squeezed out from the specimens during hot pressing at 1600 °C under 25 MPa. Also, the formation of TiC_x by the decomposition of Ti_3AlC_2, which is confirmed by XRD study shown in Fig. 1(f), would make the grain growth difficult by acting as pinning sites.

The densities of samples hot pressed using TiC_x ($x = 0.6$)/Al powder mixtures are changed with hot pressing temperature as shown in Fig. 3. The densities of samples are increased with the hot pressing temperature up to about 1300 °C, and then it reached the theoretical density of Ti_3AlC_2, 4.25 g/cm^3. The density of sample hot pressed at 1600 °C is slightly higher than theoretical density of Ti_3AlC_2 due to the formation of TiC_x and/or TiC (density ~ 4.9 g/cm^3) by the partial decomposition of synthesized Ti_3AlC_2 at that temperature.

The results of X-ray diffraction, scanning electron microscopy, and high resolution transmission electron

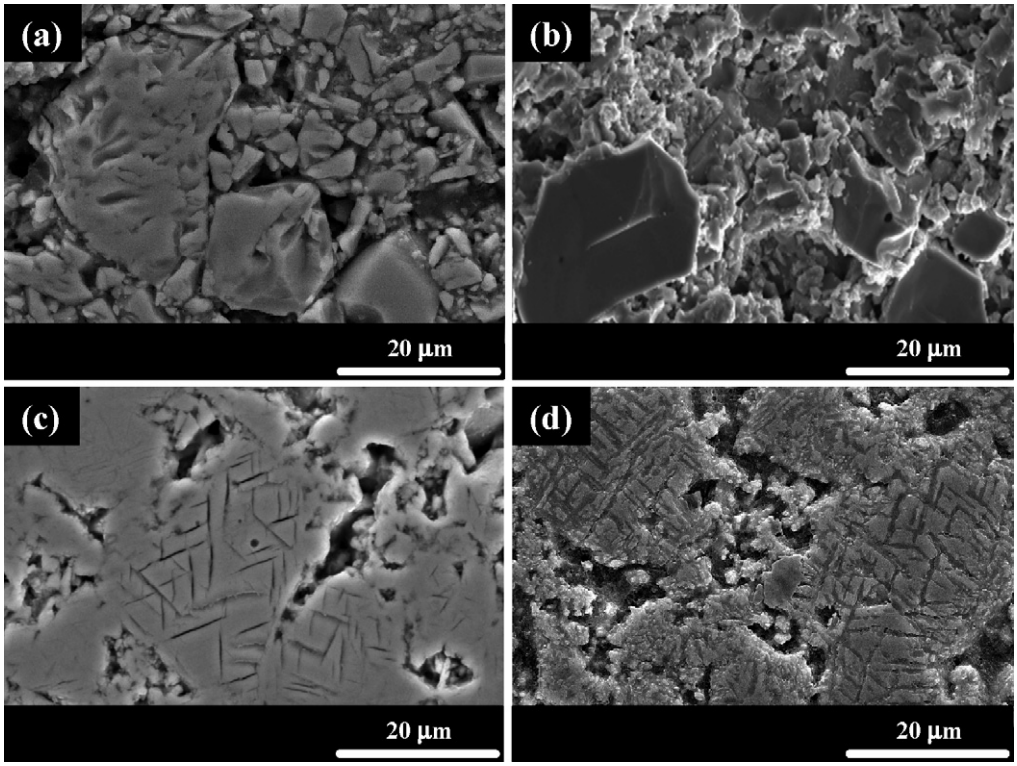

Fig. 5. SEM micrographs of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at 1000 °C for various reaction time of (a) 0 min, (b) 10 min, (c) 60 min, and (d) 240 min under 25 MPa.

microscopy of the specimen synthesized by hot pressing at 1000 °C under 25 MPa as a function of time in Ar are presented in Figs. 4–6. Fig. 4 shows XRD patterns of the specimen synthesized at 1000 °C as a function of time under 25 MPa in Ar. For the specimen instantly furnace cooled as soon as reached at 1000 °C, un-reacted TiC_x and Al were appeared as major phases with Ti_3AlC_2 and Al_3Ti as minor phases. After 10 min at 1000 °C, peak intensities of TiC_x, Ti_3AlC_2 and Al_3Ti were not notably changed, but Al peaks were diminished mostly due to the reaction with TiC_x (see Fig. 4(b)). Further increase of hot pressing time to 60 min resulted in a significant increase of contents of Ti_3AlC_2 phases with un-reacted TiC_x as a minor phase and without Al_3Ti phases, and resulted in a formation of a new crystalline phase, Ti_2AlC (see Fig. 4(d)). With further increase to 240 min, Ti_3AlC_2 became a dominant phase with only small amounts of Ti_2AlC phase which is shown in Fig. 4(d). It was found that the only small amount of TiC_x was involved in the formation of Al_3Ti during the synthesis process of Ti_3AlC_2 by hot pressing using TiC_x and Al powder mixture at 1000 °C. Al_3Ti was seemed to be formed by the reaction between molten Al and TiC_x at the surface of TiC_x particles during the early stage of the reaction. With increasing hot pressing time, Al_3Ti would react with TiC_x to form Ti_3AlC_2. As soon as Al started to diffuse into TiC_x particles, Ti_3AlC_2 were seemed to be predominantly synthesized without forming Al_3Ti as an intermediate phase. The formation of Ti_2AlC might be explained by the uneven distributions of carbon vacancies in TiC_x particles. When the reaction time is sufficiently long enough to form Ti_3AlC_2, Ti_2AlC will be further reacted with un-reacted TiC_y ($y > 0.6$) with relatively low vacancy concentration in TiC_x particles to form Ti_3AlC_2 as a following reaction:

$$0.8TiC_y + 1.1Ti_2AlC = Ti_3Al_{1.1}C_{1.8} \quad (y = 0.8) \tag{1}$$

Fig. 5 shows SEM microstructures of etched surfaces for the samples synthesized by hot pressing using the TiC_x ($x = 0.6$) and Al mixed powders as a function of reaction time at 1000 °C under 25 MPa in Ar. For the specimen synthesized at 1000 °C for 0 min and 10 min corresponding to Fig. 4(a) and (b), un-reacted TiC_x particles and Al are dominant phases with small amount of Al_3Ti and Ti_3AlC_2, which can be assumed with results of

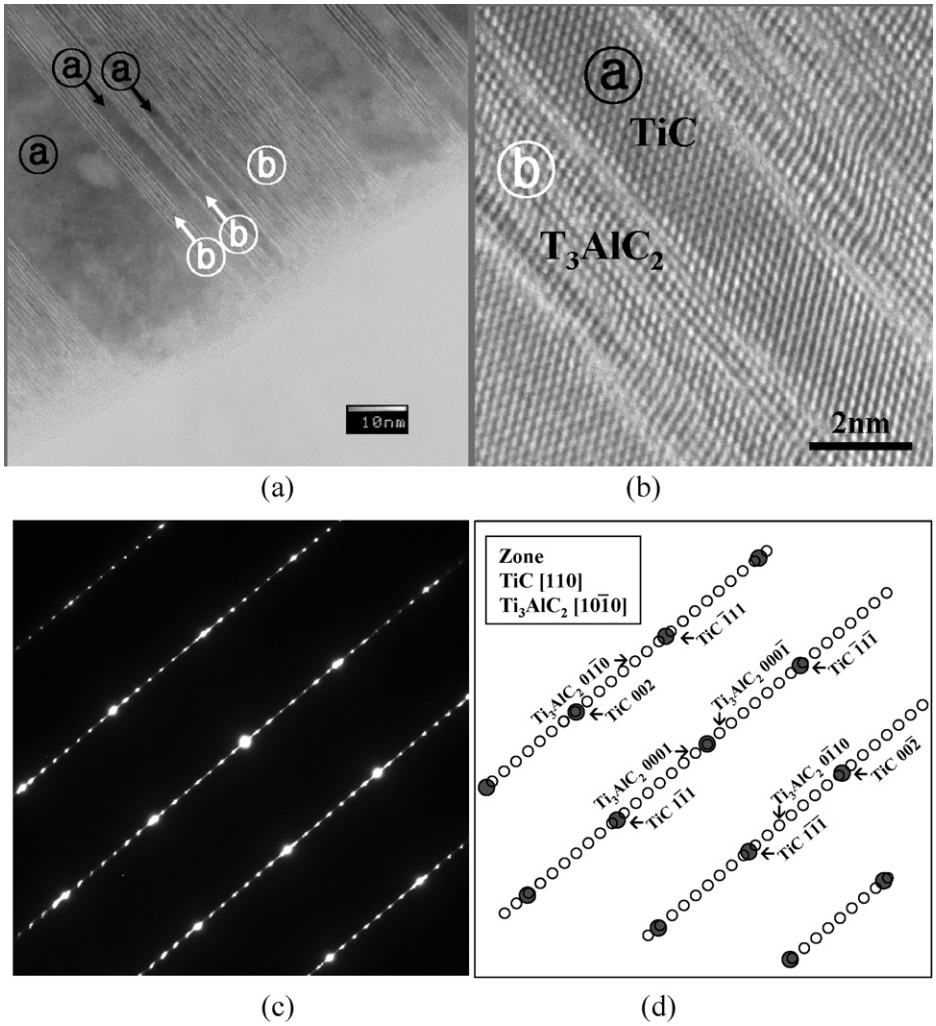

Fig. 6. TEM micrographs of the synthesized Ti_3AlC_2 by hot pressing at 1000 °C for 60 min: (a) TEM HR image; (b) enlarged image of (a); (c) SAED patterns on region (a); (d) indexing of SAED patterns.

XRD study given in Fig. 4(a) and (b). With increasing the synthesis time shown in Fig. 5(c) and (d), needle-like (striped) etching patterns were observed in synthesized Ti_3AlC_2 particles. Fig. 6 represents the result of TEM study for formation of Ti_3AlC_2 synthesized by reaction between TiC_x and Al powder at 1000 °C for 1 h under 25 MPa. Fig. 6(a) and (b) shows high resolution TEM images in which two distinctively different regions indicated with letters "a" and "b". Phases "a" and "b" were identified as TiC_x and Ti_3AlC_2, respectively, and the phases are confirmed by selected area electron diffraction (SAED) images presented in Fig. 6(c) and (d). According to the TEM study, it is assumed that the striped etching patterns appeared in SEM microstructures would be occurred by preferred etching either the phase boundaries between TiC_x and Ti_3AlC_2 or grain boundaries in synthesized Ti_3AlC_2. As shown in Fig. 5, the density of striped etched patterns was appeared to be increased with the synthesis time, which may be due to the development of new Ti_3AlC_2 grains and increase of twin boundaries of synthesized Ti_3AlC_2. The densification of synthesized Ti_3AlC_2, however, has not been completed at 1000 °C even after holding for 4 h. Moreover, the shape of synthesized Ti_3AlC_2 was not changed much comparing to that of un-reacted TiC_x powder at this condition. Therefore, densification of synthesized Ti_3AlC_2 by the reaction with TiC_x and Al depends upon not only pressure and time, but also strongly on temperature.

Fig. 7 shows XRD patterns of the specimen synthesized using the TiC_x ($x = 0.6$) and Al powder mixture by a hot pressing at 1250 °C as a function of the synthesis time (0–240 min) under 25 MPa. As shown in Fig. 7(a), the specimen instantly furnace cooled as soon as reached at 1250 °C was found to be consisting of mainly Ti_3AlC_2 with small amounts of TiC_x and Ti_2AlC. With increasing the hot pressing time, amounts of TiC_x was reduced, but the amounts of Ti_2AlC was consistent with time. For the specimen hot pressed for 240 min at 1250 °C, TiC_x phase was not observed, but Ti_2AlC phase was remained as a miner phase. Ti_2AlC may need more time for the reaction with residual

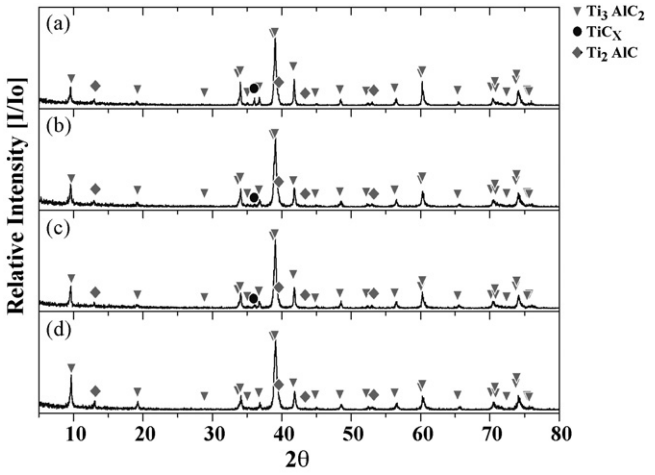

Fig. 7. XRD patterns of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at 1250 °C for various reaction time of (a) 0 min, (b) 15 min, (c) 60 min, and (d) 240 min under 25 MPa.

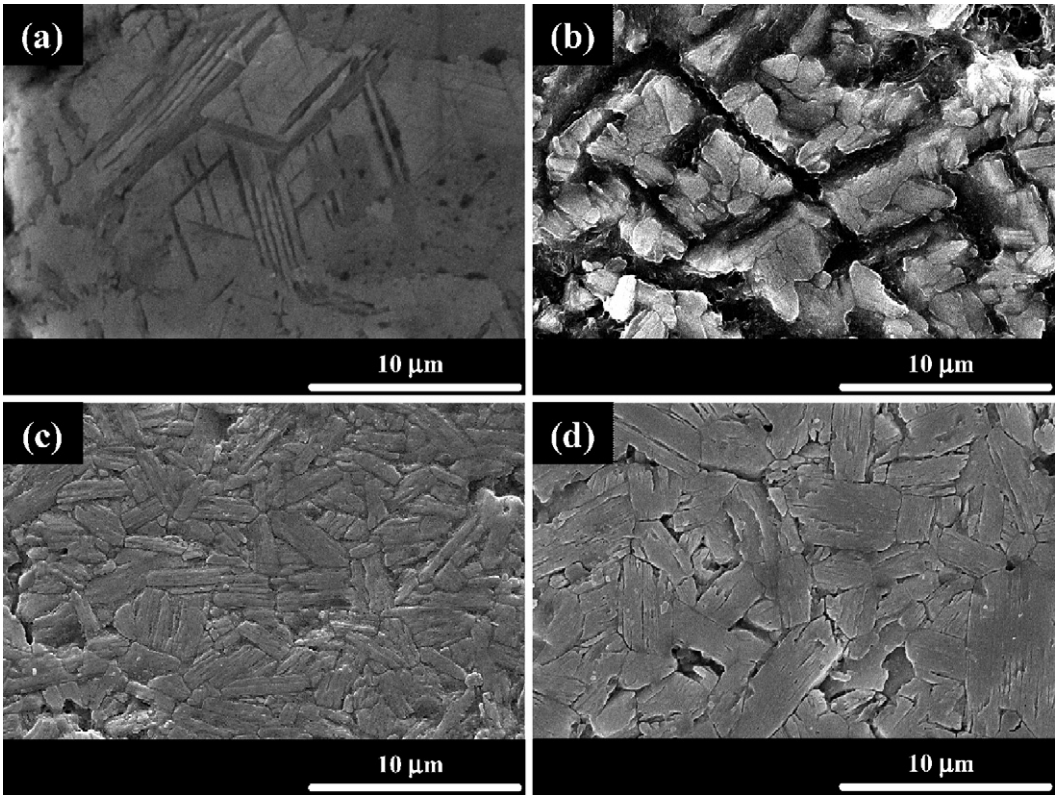

Fig. 8. SEM micrographs of the samples hot pressed using TiC_x ($x = 0.6$) and Al powder mixture at 1250 °C for various reaction time of (a) 0 min, (b) 15 min, (c) 60 min, and (d) 240 min under 25 MPa.

TiC_x to form Ti_3AlC_2 at 1250 °C. Fig. 8 shows SEM microstructures of etched surface for the samples synthesized using TiC_x ($x = 0.6$) and Al powder mixture by a hot pressing at 1250 °C as a function of hot pressing time (0–240 min) under 25 MPa in Ar. For the specimen instantly furnace cooled as soon as reached at 1250 °C, striped etched patterns were observed as shown in Fig. 8(a), which were appeared similar to those observed in the specimen hot pressed at 1000 °C for 240 min. With increasing a hot pressing time to 15 min, Ti_3AlC_2 grains were clearly visualized with a size less than 2 μm as shown in Fig. 8(b). Since XRD patterns in those two specimens were not different from each other, the sudden change in microstructure of synthesized Ti_3AlC_2 might be due to the rearrangement of synthesized Ti_3AlC_2 grains. With progress of hot pressing, the densification and the grain growth of synthesized Ti_3AlC_2 were simultaneously occurred as shown in Fig. 8(c) and (d). A density of the samples synthesized by a hot pressing using TiC_x ($x = 0.6$)/Al powder mixture was sharply increased when hot pressing time was increased to 60 min as shown in Fig. 9. The relative density of synthesized bulk Ti_3AlC_2 by hot pressing at 1250 °C for 240 min was found to be close to the theoretical density of Ti_3AlC_2. Previous study has been reported that brittle-ductile transition temperature (BDTT) of Ti_3AlC_2 is in the range of 1000–1050 °C.[1,11] Plastic deformation of Ti_3AlC_2 under compression could be occurred at elevated temperatures, and the densification of synthesized Ti_3AlC_2 seemed to be enhanced by a plastic deformation by hot pressing at the temperature above BDTT. In this study, we have obtained a theoretical density of Ti_3AlC_2 at 1250 °C under 25 MPa. As a result, it is presumed that plastic deformation of Ti_3AlC_2 could be successfully took place at 1250 °C under the pressure used in this study (25 MPa).

Fig. 10 shows the variation of flexural strength and fracture toughness of polycrystalline bulk Ti_3AlC_2 synthesized using TiC_x/Al powder mixture as a function of hot pressing temperature. As shown in Fig. 1, the synthesized bulk Ti_3AlC_2 samples by hot pressing are consisting mainly of Ti_3AlC_2 and small amount of Ti_2AlC and TiC_x except the synthesized sample at 800 °C. The flexural strengths (closed circle) and fracture toughness (closed square) of Ti_3AlC_2 were dramatically increased

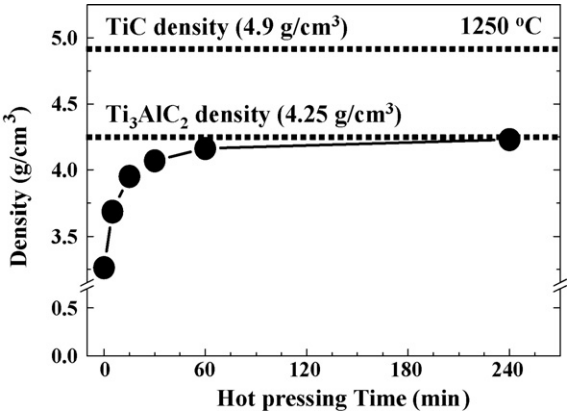

Fig. 9. Density change of samples hot pressed using TiC_x ($x = 0.6$) and Al powder at 1250 °C for 0–240 min under 25 MPa.

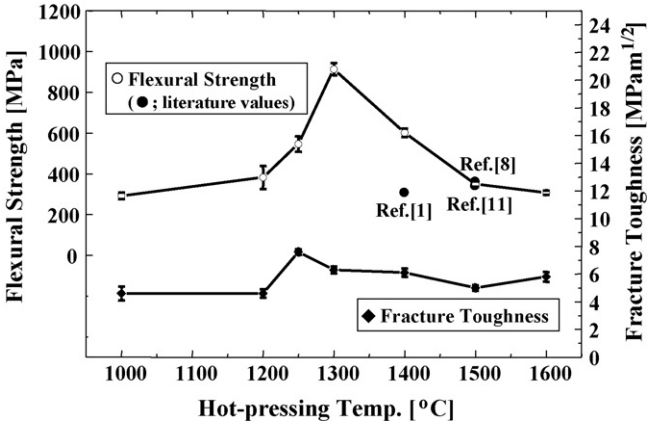

Fig. 10. Variation of flexural strength and fracture toughness of synthesized Ti_3AlC_2 as a function of hot pressing temperature.

with the hot pressing temperatures at 1300 °C and 1250 °C, respectively. Presumably, the densification of Ti_3AlC_2 at those temperatures could be a main reason for this sudden increase. The flexural strength is then significantly decreased with hot pressing temperature after it reached a peak at 1300 °C while the fracture toughness sustained the value around six after it reached a peak. The maximum flexural strength of Ti_3AlC_2 synthesized by hot pressing at 1300 °C was about 920 MPa, and the maximum fracture toughness of Ti_3AlC_2 synthesized by hot pressing at 1250 °C was as high as about 7.5 MPa $m^{1/2}$. Although fracture toughness of Ti_3AlC_2 synthesized in this study is similar to those reported in previous studies, flexural strength of Ti_3AlC_2 synthesized in this study is significantly higher than the literature values which are about 300–450 MPa. It has been known that impurities such as Ti_2AlC and TiC_x existing in Ti_3AlC_2 are beneficial to the flexural strength.[1,8,11] Interestingly, although Ti_3AlC_2 synthesized in previous studies contained impurities such as un-reacted TiC_x, Ti_2AlC, or other intermediate phases, the flexural strengths of Ti_3AlC_2 were reported below 450 MPa. Therefore, we could consider other factors improving flexural strengths of Ti_3AlC_2 in this study. The average grain size of Ti_3AlC_2 synthesized by hot pressing at 1300 °C was measured by a standard metallographic technique, and it was about 5 μm which is much smaller than the average grain size, 10–20 μm, in previous studies. Therefore, flexural strength of Ti_3AlC_2 synthesized in this study expects to be higher than literature values. However, it is not good enough to explain the dramatic increase of the flexural strength of bulk Ti_3AlC_2 synthesized at 1300 °C. In Fig. 6, it was mentioned that nano-sized Ti_2AlC and TiC_x phases were formed inside Ti_3AlC_2 phases, which may strengthen Ti_3AlC_2 effectively.[15,16] It might be another important factor to be able to explain the exceptionally increased flexural strength of Ti_3AlC_2 comparing to literature values. With increasing hot pressing temperature from 1300 °C to 1500 °C, Ti_2AlC further reacted with residual TiC_x to form Ti_3AlC_2 and the grain size of bulk Ti_3AlC_2 was abruptly changed from fine to course grain. Therefore, since two important factors deciding the flexural strength of Ti_3AlC_2 are disappeared, the flexural strength of bulk Ti_3AlC_2 synthesized above 1400 °C is significantly decreased. The representative fracture surfaces of bulk Ti_3AlC_2 synthesized by hot

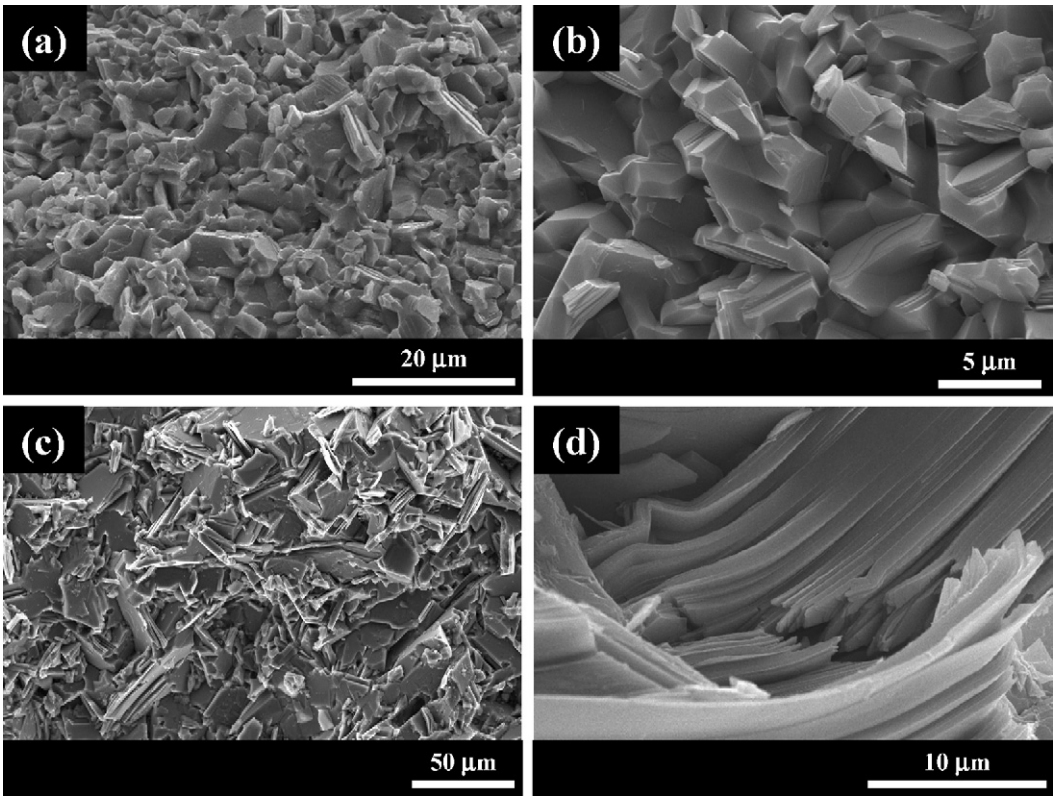

Fig. 11. SEM fracture morphologies of Ti_3AlC_2 synthesized at 1300 °C ((a) and (b)) and 1500 °C ((c) and (d)) for 1 h under 25 MPa.

pressing at 1300 °C and 1500 °C for 1 h are shown in Fig. 11. Fig. 11(b) and (d) are enlarged micrographs of Fig. 11(a) and (c), respectively. Inter-granular fracture is dominantly observed for the bulk Ti_3AlC_2 synthesized at 1300 °C while the bulk Ti_3AlC_2 synthesized at 1500 °C shows apparent transgranular fracture mode since fracture surface shows clear laminated layers. Interestingly, even though the bulk Ti_3AlC_2 synthesized at 1300 °C shows inter-granular fracture mode, the flexural strength is significantly higher than the specimen fractured in trans-granule manner (see Fig. 10). The strength of grain boundary of polycrystalline bulk Ti_3AlC_2 might be stronger than that of Ti_3AlC_2 grains which consisted of layered structure. Since the strength of Ti_3AlC_2 grains could be enhanced by reinforcement of nano-sized phases such as TiC_x and Ti_2AlC inside of the layered Ti_3AlC_2, the strength of Ti_3AlC_2 grains overwhelmed that of grain boundaries. Therefore, for bulk Ti_3AlC_2 synthesized at 1300 °C, inter-granular fracture was predominantly occurred. The nano-sized phases inside Ti_3AlC_2 grain was disappeared through further reaction between residual TiC_x and Ti_2AlC to synthesize Ti_3AlC_2 with increasing hot pressing temperature, which resulted transgranular fracture in bulk Ti_3AlC_2 synthesized above 1400 °C. The improved flexural strength of Ti_3AlC_2 synthesized at 1300 °C seems to be due to fine microstructures as well as reinforcement of in situ formed nano-sized phases such as Ti_2AlC and TiC_x.

Fig. 12 shows the variation of Vickers hardness of bulk Ti_3AlC_2 synthesized by hot pressing at 1300 °C and 1500 °C. Vickers hardness of bulk Ti_3AlC_2 was about 3.5–6 GPa and the hardness decreases with indentation load which are similar to those of other ternary carbides.[1,8,11,17,18] Vickers hardness was appeared to be higher in fine grained Ti_3AlC_2 synthesized at 1300 °C. The microstructures around Vickers indent marks of synthesized Ti_3AlC_2 under load of 100 N are shown in Fig. 13. Any of sharp indentation cracks were not observed, but quasi-plastic deformation phenomena such as layer delamination and kink band formation as well as grain pull-out were occurred around the indent mark as shown in Fig. 13(b), which would impede the crack growth at the edge of indents by effective releasing the energy for crack growth.

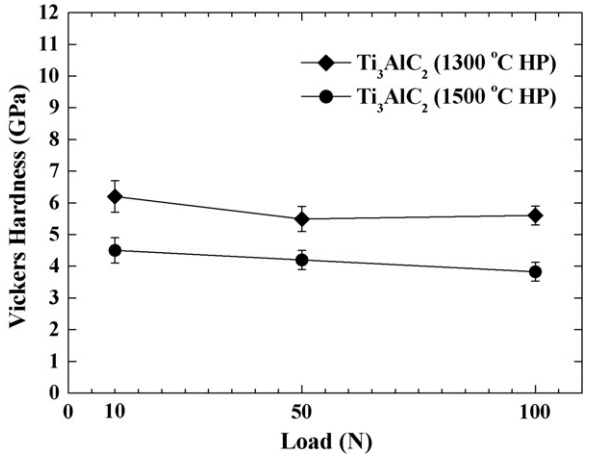

Fig. 12. Variation of Vickers hardness of synthesized Ti_3AlC_2 nano-composites as a function of indentation load.

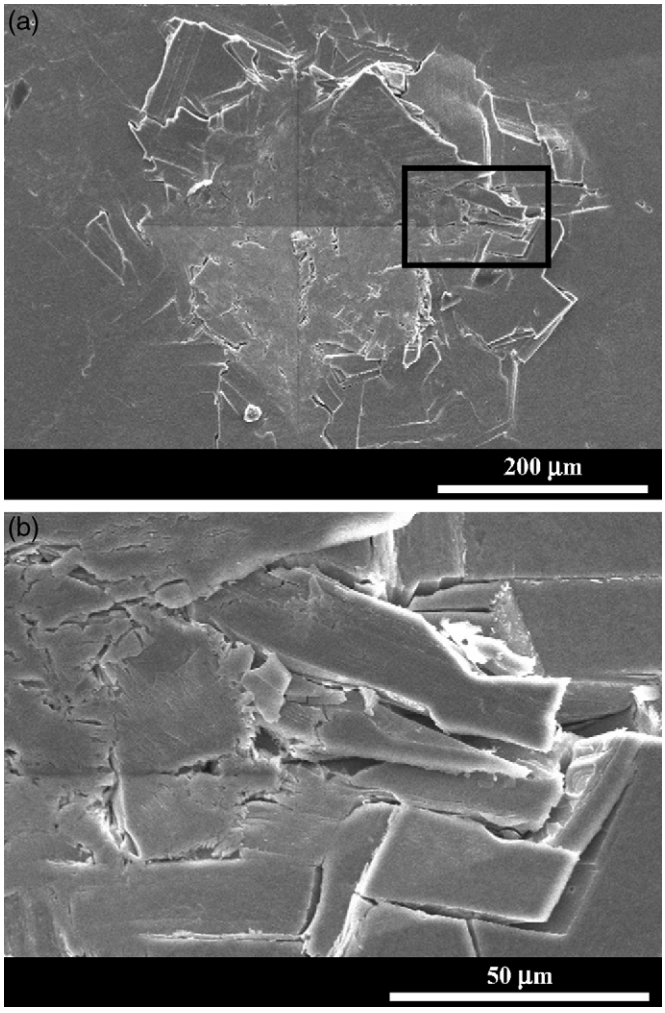

Fig. 13. (a) SEM micrographs of Vickers indents on the Ti_3AlC_2 synthesized at 1500 °C. (b) Is an enlarged microstructure of square in (a).

4. Conclusions

Polycrystalline Ti_3AlC_2 was successfully synthesized by hot pressing from TiC_x ($x = 0.6$) and Al powder mixture at the temperature above 1000 °C under 25 MPa. Time dependency of forming Ti_3AlC_2 was also investigated. Ti_3AlC_2 was immediately synthesized at 1000 °C with small amount of Al_3Ti. After about 4 h at 1000 °C, Ti_3AlC_2 became a dominant phase with small amount of Ti_2AlC. With increasing hot pressing time at the temperature of 1000–1250 °C, the kinetics of synthesizing Ti_3AlC_2 was faster and it became a predominant phase in a short period of time. The densification of Ti_3AlC_2 was examined as a function of hot pressing time and temperature. Near fully dense Ti_3AlC_2 was synthesized above 1250 °C in 1 h and fully dense and relatively pure Ti_3AlC_2 was obtained at 1250 °C after 4 h holding and above 1400 °C in a short period of holding time. The resulting Ti_3AlC_2 showed the typical laminated structure of ternary carbides. By TEM study, the formation of nano-sized TiC_x and Ti_2AlC phases in Ti_3AlC_2 phases was investigated. And, the existence of the nano-phases in Ti_3AlC_2 is assumed to be a strengthening factor of the specimen. It was found that elongated grain structure of Ti_3AlC_2, which was stable until 1500 °C, was not stable at 1600 °C that might be occurred by partial melting of Ti_3AlC_2.

Fracture toughness of Ti_3AlC_2 synthesized in this study is similar to those reported in previous studies. The maximum flexural strength of synthesized bulk Ti_3AlC_2 was over 900 MPa. Flexural strength of Ti_3AlC_2 synthesized in this study is significantly higher than the literature values which are about 300–450 MPa. It could be explained by the reinforcement of nano-sized phases such as residual TiC_x and Ti_2AlC in Ti_3AlC_2 phase and smaller average grain size. Nano-sized reinforcement of residual TiC_x and Ti_2AlC intermediate phase phases in Ti_3AlC_2 phase was possible by synthesizing Ti_3AlC_2 using TiC_x and Al powder mixture used in this study. The flexural strength was then significantly decreased with hot pressing temperature. Grain coarsening might be the main reason of the decrease in flexural strength. The Vickers hardness of bulk Ti_3AlC_2 was about 4.5–6.5 GPa under the loading of 10 N.

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