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Synthesis and microstructure of Ti_3AlC_2 by mechanically activated sintering of elemental powders

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Abstract

The mechanically activated sintering (MAS) process has been adopted to synthesize Ti_3AlC_2 by using Ti, Al and graphite elemental powders. These were subjected to mechanical alloying with charge ratios (CR) of 20:1 and 50:1, respectively. Fine powders containing TiC, Ti_3AlC_2 and Al_3Ti were obtained after milling for 4 h with a CR of 20:1, and for 1.5 h with a CR of 50:1. The mechanical alloyed (MAed) powders were pressureless sintered at different temperatures. Ti_3AlC_2 started to form at 1250 °C and its content increased at 1350 °C. However, it decomposed to TiC at 1450 °C. The microstructure of sintered samples showed that many Ti_3AlC_2 grains were delaminated and broken. Some severely delaminated Ti_3AlC_2 grains in which kink bands developed were also found.

Keywords: A. Milling; A. Sintering; B. Microstructure; Ti_3AlC_2

1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) has been proved to combine the best properties of both metals and ceramics. For example, it has low density, high modulus of elasticity, high strength at high temperatures, good workability, non-susceptibility to thermal shock, good oxidation resistance, excellent thermal and electrical conductivity, etc. [1,2].

Till now, many sintering methods such as hot isostatic pressing (HIP) [1], hot pressing (HP) [2], spark plasma sintering (SPS) [3], combustion synthesis (CS) [4], self-propagating high temperature synthesis (SHS) [5], have been developed to fabricate Ti_3AlC_2. However, the sintering temperature and pressure were higher, and the sintering time was longer for synthesizing Ti_3AlC_2 by using the above methods. From an industrial point of view, it is necessary to develop a new method to prepare this material in relatively short time and low temperature.

Recently, the mechanically activated sintering (MAS) process, including a combination of mechanical alloying the mixed powder to a superfine structure (1st step) followed by sintering (2nd step) [6], has attracted much interest, because it has been used to synthesize various materials with homogeneous and nano microstructure. For example, TiC reinforced Ti–Al composite [7], SiC in situ reinforced $MoSi_2$ composite [8], TiB_2–TiC composite [9] and TiB_2–TiN composite [10] all have been synthesized by using the MAS process. Furthermore, the milled powders consist of many fine particles with large grain boundary areas; the buildup of defects and the formation of internal strains improve the sinterability, thus the sintering temperature decrease.

Main purpose of this work is to adopt the mechanically activated sintering technique to synthesize Ti_3AlC_2 and discuss the effects of the MAS parameters on the formation of Ti_3AlC_2.

2. Experimental procedures

Ti (average particle size: 48 μm, >99% purity), Al (particle size: <75 μm, >99% purity) and C (graphite, average particle size: 45 μm, >99% purity) powders were used in this experiment. Mechanical alloying was carried out in a planetary ball mill (QM-1SP4) with stainless steel containers and balls. The powder mixtures were charged into 500 mL-containers with a stoichiometric mole ratio of 3:1:2. Then the containers were evacuated by a pump. The rotation speed of the containers was set as 500 rpm. The weight ratios of ball to powder (also

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called charge ratio, CR) were 20:1, 50:1. A small amount of milled powders was taken out from the containers after selected milling times for X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observations, and then the containers were re-evacuated and the milling process was performed continuously. XRD analysis was made using a D/Max-rB diffractometer at 40 kV and 20 mA with Cu Kα radiation. The morphology of powders was observed by SEM (model: STEREOSCAN 360) equipped with energy-dispersive spectroscopy (EDS).

The MAed powders were cold pressed under 200 MPa to form compacts with a diameter of 10 mm and a height of about 5 mm. The compacts were put into a graphite crucible and then pressureless sintered at different temperatures for 1 h at vacuum. The sintered samples were then characterized by XRD and SEM.

3. Results and discussion

Fig. 1 shows the XRD patterns of the powders after different milling time. Fig. 1(a) is the pattern of the Ti, Al and C mixtures before milling, Fig. 1(b) and (c) are the patterns of the powders after milling for 3 h and 4 h, respectively, with CR = 20:1, however, Fig. 1(d) is the powder after milling for 1.5 h with CR = 50:1. The peak belonging to graphite disappears completely after milling for 3 h, and the Al peaks other than (1 1 1) peak owing to it overlapping with Ti (0 0 2) also vanish (Fig. 1(b)). This suggests that the graphite and Al might have been transformed to amorphous phases or distributed in the grain boundaries of Ti. All peaks for Ti broaden and decrease in intensity at the same milling time, indicating the reduction of the average crystallite size, and the buildup of defects and the formation of internal strains. It should be noted that new phases, i.e. TiC, Ti_3AlC_2 and Al_3Ti, are found after milling for 4 h with CR = 20:1. The appearance of the new phases indicates that a mechanically induced self-propagating reaction (MSR) is triggered during mechanical alloying of Ti–Al–C the powders, in which a defined critical state is reached after a repeated fracture and cold welding process. However, the same phenomenon happens only after milling Ti–Al–C mixtures for 1.5 h with CR = 50:1. It is well known that CR is one of the important parameters during MA. In general, the higher the CR, the shorter is the time required to obtain the final products. With increasing milling time, the peaks belonging to Ti_3AlC_2 and $TiAl_3$ disappeared gradually, only leaving TiC with broadened peaks. No other phases were found even after the milling time was increased up to 60 h.

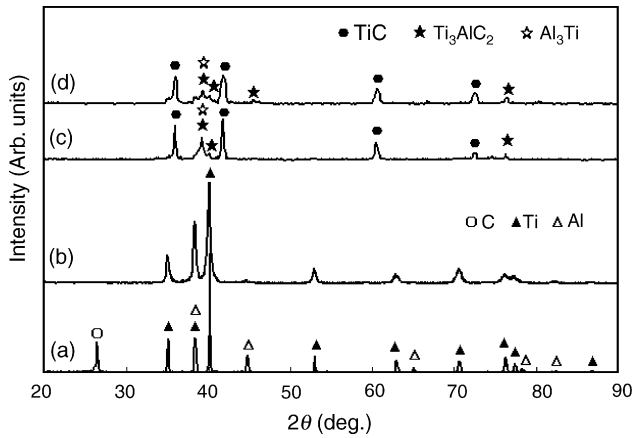

Fig. 1. XRD patterns of the powder mixtures after milling for different times: (a) 0 h, (b) and (c) are milling for 3 and 4 h, respectively, with CR = 20:1, and (d) 1.5 h with CR = 50:1.

Fig. 2 provides the morphologies of the powder mixtures after mechanical alloying. It can be clearly seen from Fig. 2(a) that the powders are mainly composed of many agglomerates formed owing to cold welding whose size is less than 20 μm and consists of much smaller particles. Careful observations reveal that each particle has a tendency to be round in shape. With increasing CR to 50:1, the particle sizes decrease faster. The agglomerates are about 1.5 μm after milling for only 1.5 h (Fig. 2(b)).

The milled powders were sintered at different temperatures. XRD results are shown in Fig. 3. Ti_3AlC_2 starts to form at 1250 °C, but TiC is the predominating phase. High content of Ti_3AlC_2 is obtained at 1350 °C, however, TiC still exists as an unwanted phase. It should be noted that the content of Ti_3AlC_2

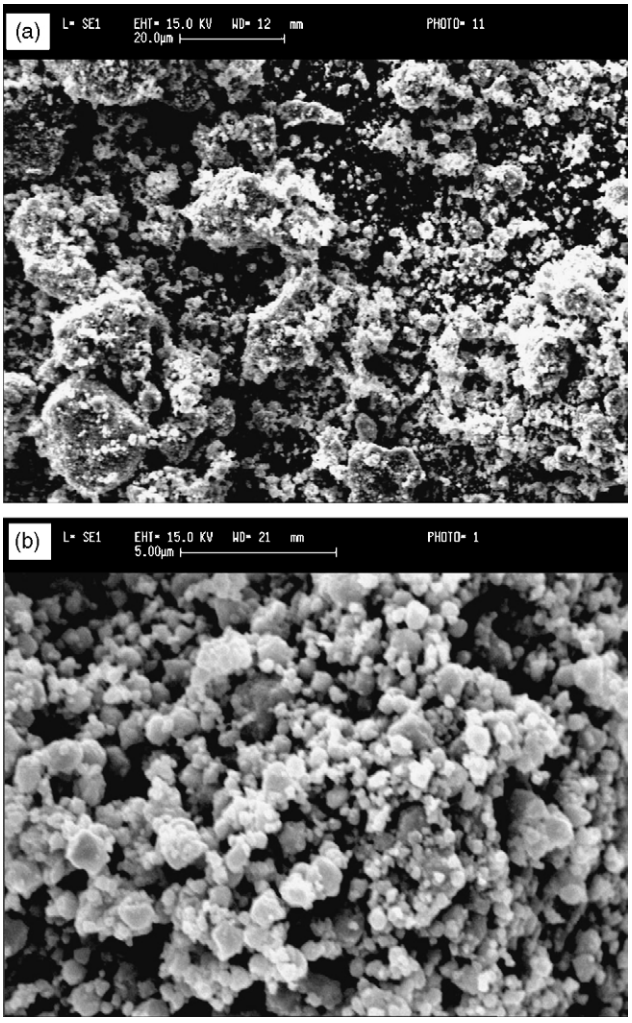

Fig. 2. SEM micrographs of the powder mixtures after milling for (a) 4 h, with CR = 20:1, and (b) 1.5 h, with CR = 50:1.

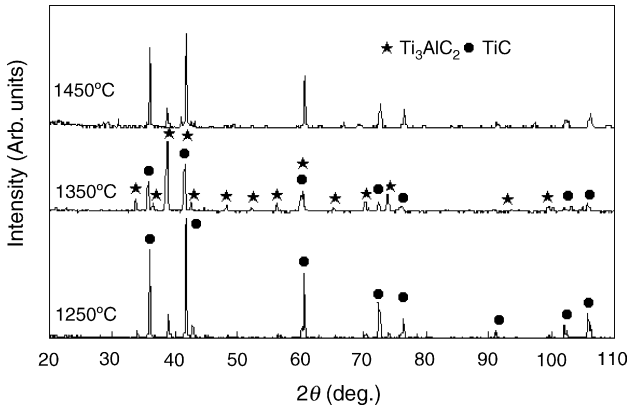

Fig. 3. XRD patterns of the sample made of powder milled for 4 h with CR = 20:1 after sintering at different temperatures for 1 h.

decreases dramatically as the temperature is increased up to 1450 °C, and TiC correspondingly increases, this suggesting Ti_3AlC_2 decomposition into TiC and Al to occur. It has been reported that Ti_3AlC_2 decomposes at 1360 °C into Al and TiC [11]. Al is not found in the XRD patterns. Most probably it evaporates from the sample at that temperature.

High content of Ti_3AlC_2 has been obtained in the sample made of the powder milled for 1.5 h with CR = 50:1 and sintered at 1350 °C (Fig. 4). However, also in this case TiC contaminates the system. Although TiC always accompanies Ti_3AlC_2 as a by-product, pure Ti_3AlC_2 can still be achieved by sintering the powder with a slight excess of Al after an appropriate milling time to reach a defined critical state for forming a nanostructured powder without TiC formation.

From Figs. 3 and 4, it can be observed that no impurities such as Fe or other compounds exist. Thus, the short milling time prevents contamination of the system. However, when the powders after 60 h milling were sintered at 1350 °C, there were some Al–Ni compounds and stainless steel appearing in XRD patterns (not shown here) coming from impurities from the balls and the container after a prolonged milling time. Hence, reduction of the milling time is necessary as far as fine powders once produced.

A typical SEM micrograph from the fracture surface of a sintered sample is shown in Fig. 5. The Ti_3AlC_2 grains with plate-like shapes are about 10 μm in size (Fig. 5(a)), exhibiting two types of fracture surfaces, with layered and flat features, respectively. Both result from transgranular fracture. When the basal planes of Ti_3AlC_2 are normal to the crack propagation, the

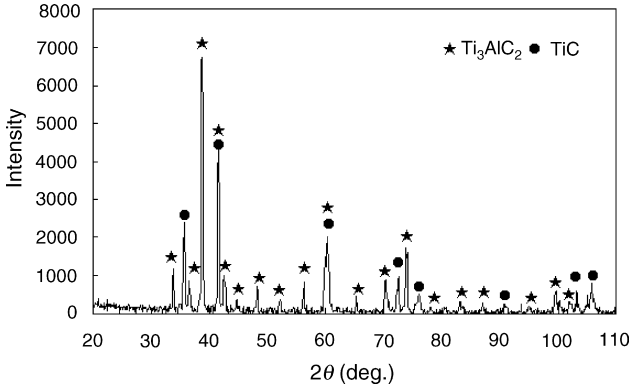

Fig. 4. XRD pattern of the sample made of powder milled for 1.5 h with CR = 50:1 after sintering at 1350 °C for 1 h.

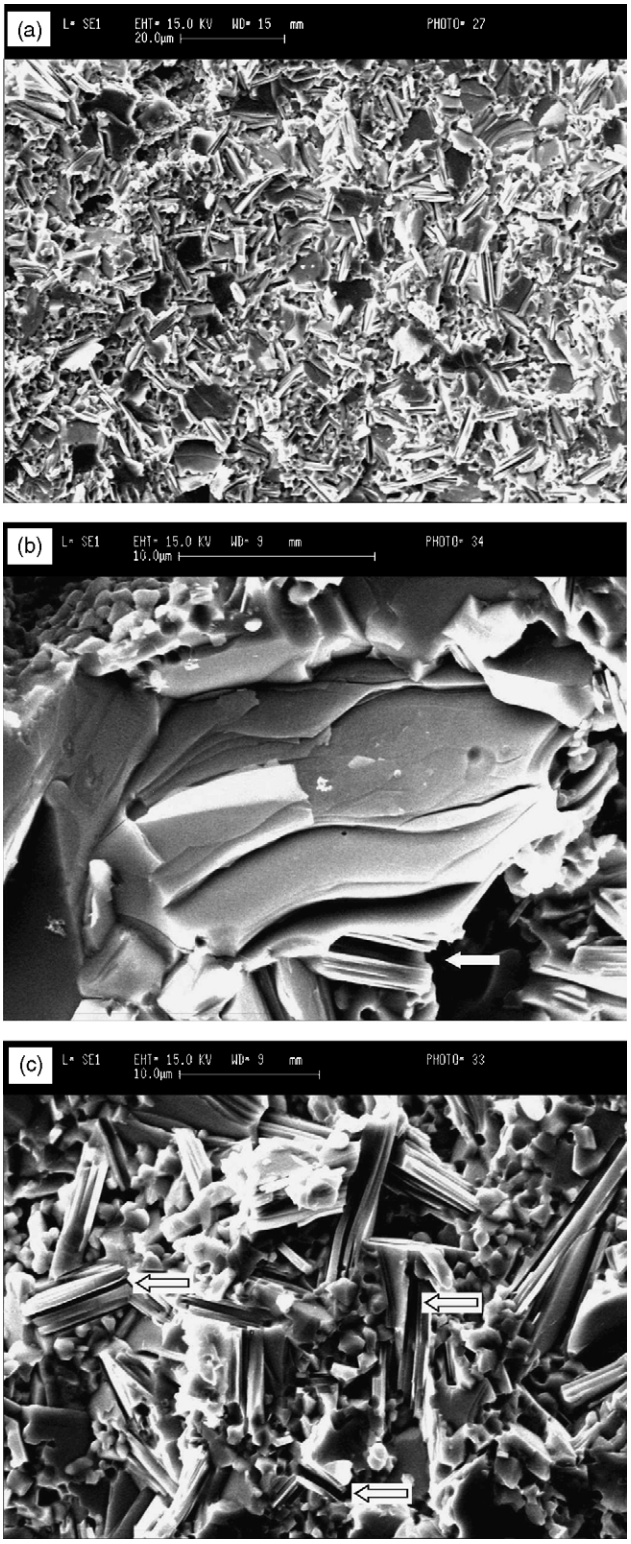

Fig. 5. SEM micrographs of the fracture surfaces of the sample made of powder milled for 1.5 h with CR = 50:1 after sintering at 1350 °C for 1 h appears in (a) to (c).

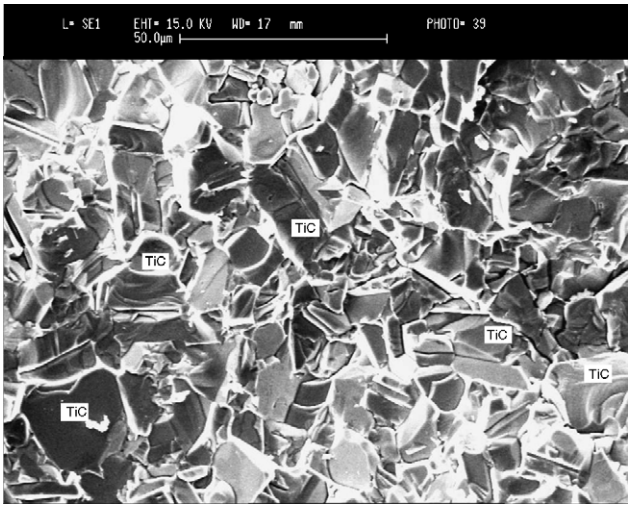

Fig. 6. SEM micrograph of the fracture surface of the sample sintered at 1450 °C for 1 h.

crack enters into the grains and then will be deflected repeatedly by the inner-layers being Ti_3AlC_2 grains composed of many nano-sized layers. When the basal planes are parallel to the crack propagation, the crack propagates along them and results in grains delamination; thus the latter feature occurs.

A larger delaminated grain with nano-sized lamellas can be clearly found in Fig. 5(b). Some lamellas are broken and pulled out, leaving many long dents denoted by arrows in Fig. 5(b) and (c). This feature can exhaust the energy of crack propagation and contribute to improving the mechanical properties of Ti_3AlC_2 materials.

However, at 1450 °C, a different microstructure appears (Fig. 6). Larger TiC particles are present with polyhedral shape, whereas some TiC particles still exhibit the layered feature. The latter feature means that TiC must be formed at the expense of the Ti_3AlC_2 grains.

Furthermore, some severely delaminated grains with kink band formation can also be found in Fig. 7. The kink bands can be observed clearly in the enlarged zone (Fig. 7(b)). Fig. 7(b) and (c) show that the curvature of the kinked part is very sharp, but not broken. The deformation of Ti_3AlC_2 grains combining the formation of the kink bands and delamination is unusual for ceramics. This buckling and delamination must redistribute the strain and dissipate the stress concentration, which gives Ti_3AlC_2 a damage-tolerance capability. The above feature provides another evidence for confirming the room-temperature plasticity as previously reported [1,2]. The mechanism of formation of kink bands for Ti_3AlC_2 is similar to the one for Ti_3SiC_2, which is discussed in detail in references [12–14].

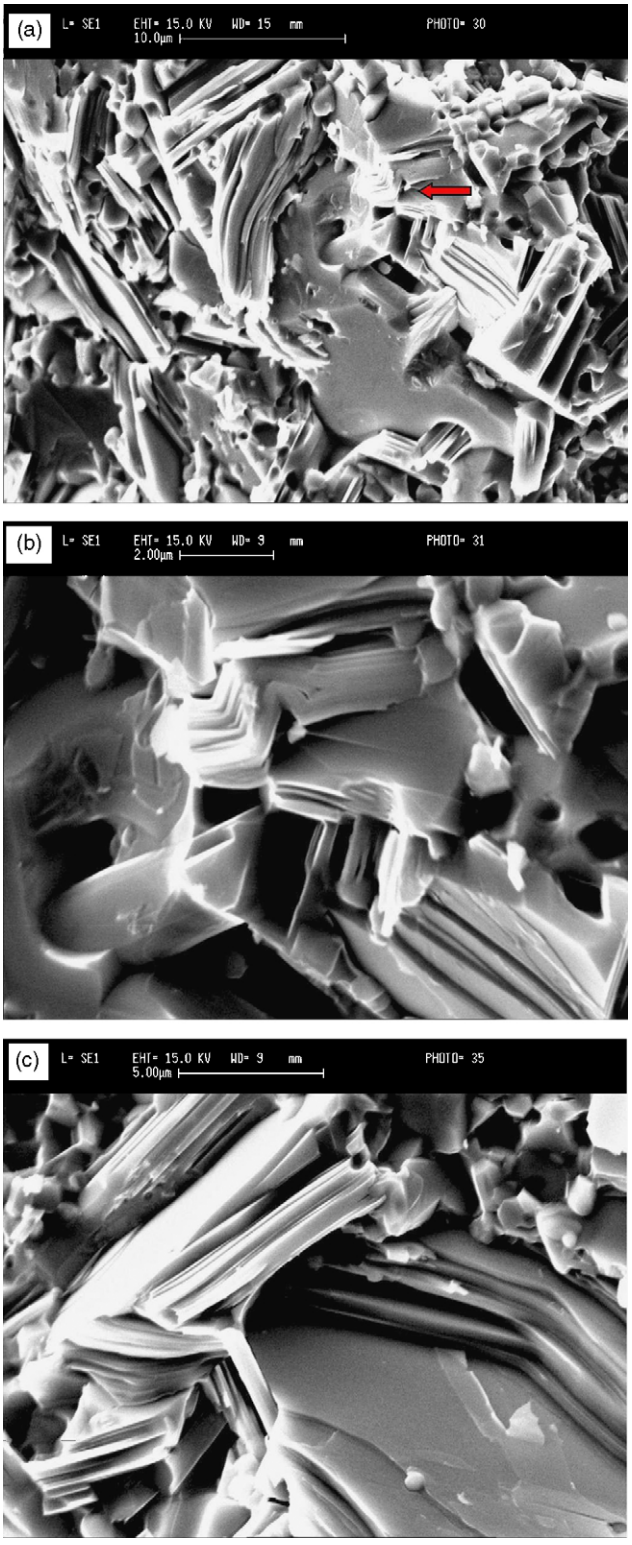

Fig. 7. SEM micrographs of the fracture surfaces of the sample made of powder milled for 1.5 h with CR = 50:1 after sintering at 1350 °C for 1 h, in which the delaminated grains with kink band formation appears in (a) to (c). (b) A high magnification micrograph taken from the marked area by arrow in (a).

4. Conclusions

Mechanically activated sintering has been adopted to synthesize Ti_3AlC_2 powders from Ti, Al and C elemental powders. From experimental evidences, the main conclusions can be summarized as follows.

(1) Fine powders containing TiC, Ti_3AlC_2 and Al_3Ti were obtained after milling Ti, Al and C elemental powders for 4 h with a CR of 20:1, for 1.5 h with a CR of 50:1. It indicates that a mechanically induced self-propagating

reaction is triggered during mechanical alloying of the Ti–Al–C powders.

(2) A short milling time is suitable for getting fine structured powders without contamination. The MAed powders do improve the sinterability because they have large grain boundary areas and short diffusion pathway. High Ti_3AlC_2 content was obtained after sintering the milled powders at 1350 °C. However, Ti_3AlC_2 decomposes to TiC and Al at 1450 °C.

(3) Some delaminated, broken and pulled out Ti_3AlC_2 grains were found. Deformed Ti_3AlC_2 grains featuring kink bands were also observed. These features can exhaust the energy of crack propagation, redistribute the strain and dissipate the stress concentration, which endows Ti_3AlC_2 damage-tolerance capability.

Acknowledgements

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References

[1] N.V. Tzenov, M.W. Barsoum, Synthesis and characterization of Ti_3AlC_2, J. Am. Ceram. Soc. 83 (2000) 825–832.

[2] X.H. Wang, Y.C. Zhou, Microstructure and properties of Ti_3AlC_2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process, Acta Mater. 50 (2002) 3141–3149.

[3] A. Zhou, C. Wang, Y. Huang, A possible mechanism on synthesis of Ti_3AlC_2, Mater. Sci. Eng. A 352 (2003) 333–339.

[4] Z. Ge, K. Chen, J. Guo, H. Zhou, Combustion synthesis of ternary carbide Ti_3AlC_2 in Ti–Al–C system, J. Eur. Ceram. Soc. 23 (2003) 567–574.

[5] M. Lopacinski, J. Puszynski, J. Lis, Synthesis of ternary titanium aluminum carbides using self-propagating high-temperature synthesis technique, J. Am. Ceram. Soc. 84 (2001) 3051–3053.

[6] E. Gaffet, M. Abdellaoui, N.M. Gaffet, Formation of nanostructural materials induced by mechanical processings, Mater. Trans. J.I.M. 36 (1995) 198–209.

[7] N.Q. Wu, G.X. Wang, W. Li, J.M. Wu, Z.Z. Li, Mechanically driven synthesis of nanophase TiC/Ti-Al composite powder, Mater. Lett. 32 (1997) 259–262.

[8] S. Jayashankar, M.J. Kavfman, In-situ reinforced $MoSi_2$ composites by mechanical alloying, Scripta Metall. Mater. 26 (1992) 1245–1250.

[9] J.W. Lee, Z.A. Munir, M. Ohyanagi, Dense nanocrystalline TiB_2-TiC composites formed by field activation from high-energy ball milled reactants, Mater. Sci. Eng. A 325 (2002) 221–227.

[10] J.L. Li, K.A. Hu, Y. Zhou, Formation of TiB_2/TiN nanocomposite powder by high-energy ball milling and subsequent heat treatment, Mater. Sci. Eng. A 326 (2002) 270–275.

[11] M.A. Pietzka, J.C. Schuster, Summary of constitutional data on the Al–C–Ti system, J. Phase Equilib. 15 (1994) 392.

[12] S.B. Li, H.X. Zhai, A soft ceramic Ti_3SiC_2 with microscale plasticity at room temperature, Key Eng. Mater. 280–283 (2005) 1343–1346.

[13] S.B. Li, L.F. Cheng, L.T. Zhang, Identification of damage tolerance of Ti_3SiC_2 by hardness indentations and single edge notched beam test, Mater. Sci. Tech. 18 (2002) 231–233.

[14] M.W. Barsoum, T. El-Raghy, Room temperature ductile carbides, Metall. Mater. Trans. A 30 (1999) 363–369.