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Influence of mechanical alloying on Ti_3SiC_2 formation via spark plasma sintering technique from Ti/SiC/C powders

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Abstract

Ti_3SiC_2 was elaborated by two different methods: (i) Spark plasma sintering of 5Ti/2SiC/C powders and (ii) mechanical alloying of powders followed by Spark plasma sintering. The results showed that mechanical alloying was not advantageous for pure Ti_3SiC_2 formation but it can significantly improve the density of the obtained bulk material via the particles refinement as well as the microhardness by increasing the TiC content. It was found that the relative density was increased up to 98.58% for the sintered mechanically alloyed sample whereas it was not more than 96.04% for the sintered 5Ti/2SiC/C starting powders. The Vickers microhardness measured for both bulk samples demonstrates a high improvement for the previously mechanically alloyed powder mixture, as it was of about 1282 Hv and only 581.2 Hv for the alloy obtained from 5Ti/2SiC/C starting powders.

Keywords: C. Hardness; Ti_3SiC_2; Mechanical alloying; Spark plasma sintering technique

1. Introduction

Ternary compound Ti_3SiC_2 has received more and more attention due to its remarkable combination of the best properties of ceramic and metals and particularly the stable mechanical and electrical behavior at high temperature. In fact, like metals it is a good electrical and thermal conductor, easily machinable, relatively soft and highly thermal shock resistant. Like ceramics, it is very stiff, oxidation resistant and stable to at least 1700 °C [1–6].

Moreover, Ti_3SiC_2 has the individual combination of strength and ductility at elevated temperatures as well as resistance to thermal shock and excellent machinability that has never been observed in other materials [7]. This extraordinary grouping of properties makes Ti_3SiC_2 to be thought about as a promising material for many important industrial applications.

Therefore, it is important to make fully dense bulk Ti_3SiC_2 samples with high purity. Zhou et al. [8] were the first who synthesized the ternary compound via chemical reaction between TiH_2, Si and graphite at 2000 °C, followed by the work of Nickl et al. [9] by using the chemical vapour deposition (CVD) method. During the last decades diverse methods have been employed for the synthesis of bulk Ti_3SiC_2 such as arc melting [10], hot isostatic pressing (HIP) [11], hot pressing (HP) [12], reactive sintering [13], heat treatments in vacuum [14] and others. However, the synthesis process of all these mentioned techniques are either much time consuming or involving high pressure and high temperature.

The spark plasma sintering technique (SPS) also called the pulse discharge sintering (PDS) method, a relatively newly developed technique, has several advantages over similar processes. Indeed, with the help of this sintering method, materials can be sintered or synthesized at lower temperature and with shorter soaking time thus avoiding any exaggerate grain growth. Therefore metals and ceramic can be obtained with fine particles leading to materials

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with superior properties [15]. There are several reported works on the simultaneous synthesis and consolidation of Ti_3SiC_2 through the SPS process starting from different powder mixtures including: Ti/Si/C [16,17], Ti/SiC/C [17], Ti/Si/TiC [17,18] and Ti/SiC/TiC [19].

Nevertheless, regardless of the several starting powder mixtures cited above a single phase is often difficult to be obtained and TiC, SiC and/or Ti_5Si_3 and $TiSi_2$ inevitably appear after the synthesis.

Mechanical alloying is a low cost process appropriate to the formation of a big variety of powder materials. Furthermore, it is considered to be the most powerful technique for synthesizing nanocrystalline carbide materials at room temperature [20–22]. Nevertheless, high purity of Ti_3SiC_2 ceramic is difficult to synthesize via mechanical alloying alone [23].

In recent years, more and more attention has been paid to mechanical alloying in order to fabricate Ti_3SiC_2 because using highly deformed and reactive powders could reduce the sintering temperature and the holding time [24].

Liang and co-workers [25] obtained high purity of Ti_3SiC_2 through the combination of mechanical alloying and SPS (MA–SPS) at a temperature 300 °C lower than that reported in the literature. They obtained full dense Ti_3SiC_2 with a purity of 99.3% by adding an appropriate amount of Al and starting from the powders mixture of 3Ti/Si/2C.

Zhang et al. [26] established that Ti_3SiC_2 can be rapidly synthesized using the pulse discharge technique starting from Ti/SiC/C powder mixture at a relatively low temperature of 1250–1300 °C under a pressure of 50 MPa. They demonstrated that by adjusting the molar ratio of the starting composition to 5:2:1 the purity of Ti_3SiC_2 could be improved to about 93%.

From the synthesis processes as well as the starting composition used in the past for Ti_3SiC_2 elaboration, it is found that the purity of Ti_3SiC_2 could be further improved by adding an excess of Si to the starting powders [16]. The previous results [26] showed that a high purity of Ti_3SiC_2 could be obtained by SPS using an optimum temperature that ranges between 1250 and 1300 °C, a short soaking time of 15 min under a constant pressure of 50 MPa.

The objective of this work is to study the mechanical alloying (MA) effect on Ti_3SiC_2 purity using the SPS technique starting from a powders mixture of Ti/SiC/C at a molar ratio of 5:2:1. Two synthesis processes will be adopted in this work: direct spark plasma sintering (SPS) of Ti, SiC and C powders and the sintering of the previous mechanically alloyed powder mixture of Ti/SiC/C (MA–SPS). A comparison will be completed between the two processes in terms of Ti_3SiC_2 purity and the mechanical properties of the obtained bulk materials as well as their relative densities.

2. Experimental details

Starting powders of coarse Ti (< 40 μm, 98%, Prolabo), C (99%, Fischer Scientific) and SiC (< 44 μm, 99%, Alfa Aesar) were used in this study. The powder mixtures were placed into a shaker for 48 h for better homogeneity and the stoichiometric molar ratios were fixed at 5:2:1. The mechanical alloying procedure was conducted at room temperature using the Pulverisette 7 planetary ball mill. The Ti/SiC/C powders were sealed into stainless steal vials (45 ml in volume) with 5 stainless steal balls (15 mm in diameter) in a glove box under argon protective atmosphere. The ball-to-powder weight ratio was about 67:2. The powder mixtures were mechanically alloyed for 6 h with a rotation speed of 350 rpm. The starting powder mixture of 5Ti/2SiC/C and the previously mechanically alloyed one were respectively referred to as M1 and M2 samples.

In order to study the mechanical alloying effect on the mechanical properties of the powder mixtures, the starting powder mixtures as well as the alloyed ones were consolidated as pellets, by spark plasma sintering using an SPS-515 S SYNTEX apparatus. Based on the previous results [26], the temperature was set to 1300 °C at a heating rate of 60 °C/min. The soaking time was fixed to 10 min under a constant pressure of 64 MPa.

Before the SPS process, all the powders were well mixed during 48 h in a shaker. The powders were then, compacted into a graphite die of 8 mm in diameter and sintered in vacuum at fixed temperature of 1300 °C and pressure of 64 MPa. The soaking time at the maximum temperature was within 10 min. A constant heating rate of 60 °C/min was employed during all the sintering process. During the SPS process, the pressure was set to 54 MPa during the first 500 s. Then it was increased to 64 MPa and remained constant between 600 and 1800 s (Fig. 1). The temperature was maintained constant around 600 °C until 500 s and then increased to 1300 °C and remained constant after 1150 s until 1750 s (Fig. 2).

The starting powders as well as the bulk samples were characterized by X-ray diffraction (XRD) using a (θ–2θ) Panalytical XPERT PRO MPD diffractometer operating with Cu Kα radiation (λ=0.15406 nm). The existing

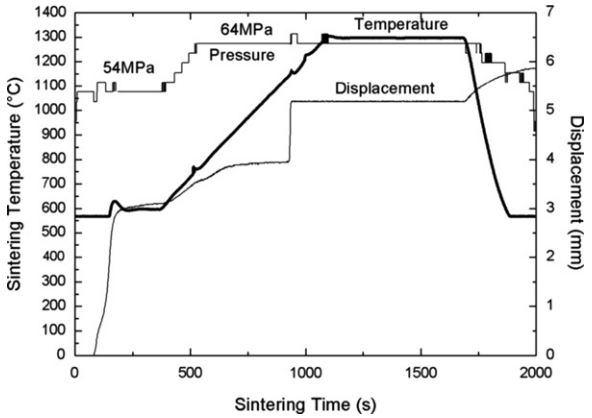

Fig. 1. Variation of sintering temperature, sample shrinkage and applied pressure during the SPS process for Ti/SiC/C powder mixture (M1) heated at 1300 °C for 10 min. Left *y*-axis corresponds to the sintering temperature and right *y*-axis corresponds to shrinkage curve.

phases were determined by the High Score Plus program based on the ICDD PDF2 data base. The formed phase proportions were determined by the FullProf program [27] using the Rietveld method [28]. The morphology and microanalysis of each synthesized alloy were carried out using the FEI Quanta 200 environmental scanning electron microscope coupled with EDAX microanalyser.

The relative densities of the consolidated samples were determined by the Archimedes' method using O-xylene as measuring liquid (density of 0.88 at 25 °C).

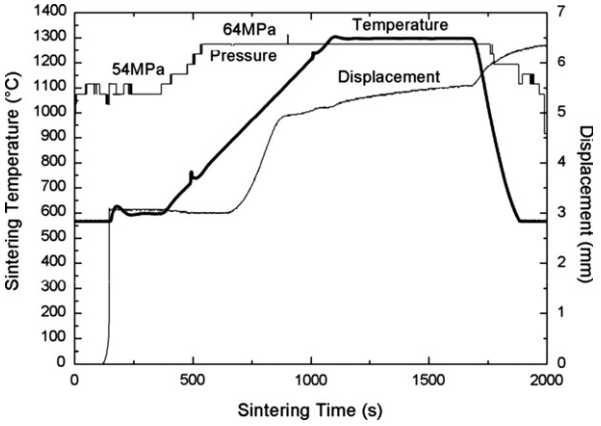

Fig. 2. Variation of sintering temperature, sample shrinkage and applied pressure during the SPS process for mechanically alloyed Ti/SiC/C powder mixture (M2) heated at 1300 °C for 10 min. Left *y*-axis corresponds to the sintering temperature and right *y*-axis corresponds to shrinkage curve.

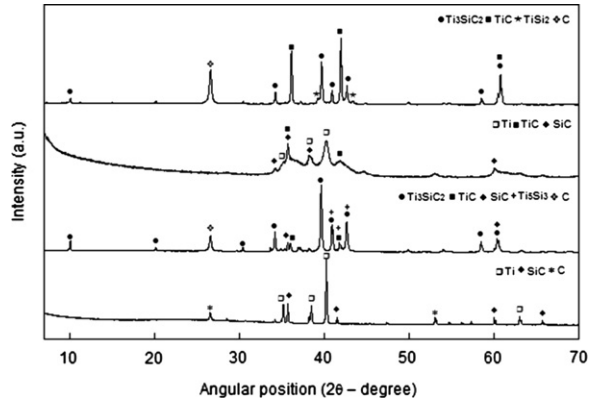

Fig. 3. XRD patterns of (a) 5Ti/2SiC/C powder mixture (M1), (b) spark plasma sintered 5Ti/2SiC/C mixture, (c) mechanically alloyed 5Ti/2SiC/C mixture (M2) and (d) spark plasma sintered mechanically alloyed 5Ti/2SiC/C mixture.

Microhardness measurements were conducted on the pellets' plane using a Duramin 20 Vickers device under a test force of 4.91 N for 7 s. Ten measurements were taken for each reported Vickers hardness value. Images of the damage induced by the Vickers indentation marks were recorded using the Park Systems XE-70 atomic force microscope by adopting the noncontact mode.

3. Results and discussion

3.1. SPS process

The displacement profiles recorded respectively as a function of pressure and temperature during the SPS

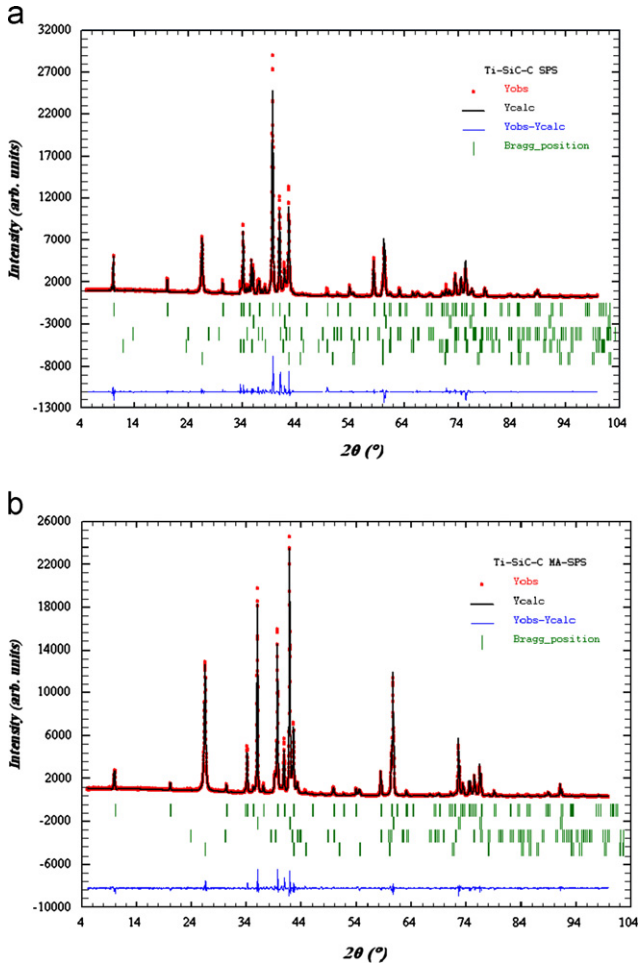

Fig. 4. Example of Fullprof program fit of (a) M1 and (b) M2 samples after SPS sintering.

Table 1
Weight contents (%) of the different phases before and after SPS process.

	Ti	SiC	C	Ti_3SiC_2	TiC	$TiSi_2$	Ti_5Si_3
M1	62.5	25	12.5	–	–	–	–
M1 SPS	–	6.58	0.66	78.0	9.77	–	4.99
M2	23.86	6.75	–	–	69.40	–	–
M2 SPS	–	–	0.97	40.94	51.94	7.15	–

process of the 5Ti/2SiC/C powder mixture (M1) as well as the mechanically alloyed powders (M2) is shown in Figs. 1 and 2. For the M1 sample, the displacement increases to 3 mm during the first 285 s under the pressure effect (the temperature was too low to induce any phase transformation). This displacement is probably attributed to the particle rearrangement of the initial powder. Then, the displacement increased in two steps to 3.9 mm when the pressure reached its maximum value (64 MPa) and the temperature increased first to 750 °C and second to 920 °C. This displacement is attributed to thermal particles softening. No further increase of the displacement was observed until 1020 s despite the temperature increase. At 1020 s, when the temperature reached 1150 °C, the displacement increased rapidly to 5.2 mm as a result of a phase transformation from a less dense material to a more dense one. This phase transformation is explained by an easy matter flow in the intergranular space of the particles intimately in contact under the pressure application. Then the displacement remained constant as the material reached its maximum density at the used pressure.

The displacement profile recorded during the SPS consolidation of the M2 sample is illustrated in Fig. 2. During the first 260 s, a fast increase in the displacement to 3.1 mm under the pressure effect is noticed. This displacement is again attributed to the particle re-arrangement because the temperature is too low to induce any phase transformation. Then, the displacement remained constant until 790 s. Between 790 s and 1000 s, when the temperature was increased linearly to 1100 °C, the displacement increased progressively to 5 mm. We assume that this is related to a progressive phase transformation which started earlier, as compared to the M1 sample, as a result of the particles reactivity increase induced by the particle refinement. Then, the displacement increased progressively to 5.6 mm as the temperature reached its maximum of 1300 °C. This displacement is attributed to the densification of the new formed phases.

3.2. Microstructural and mechanical properties

Fig. 3 shows the X-ray diffraction patterns of M1 and M2 samples before and after SPS.

After the sintering of the 5Ti/2SiC/C powder mixture, Fig. 3b showed that Ti_3SiC_2 was the principle formed phase with a minor TiC and Ti_5Si_3 phases. The starting SiC phase exists with small content as compared to the initial mixture (Fig. 3a).

After mechanical alloying of the 5Ti/2SiC/C powder mixture, in addition to SiC and Ti remaining phases, the alloy was formed mainly by TiC (Fig. 3c). Indeed, as Ti has strong chemical affinity to C in low temperature solid

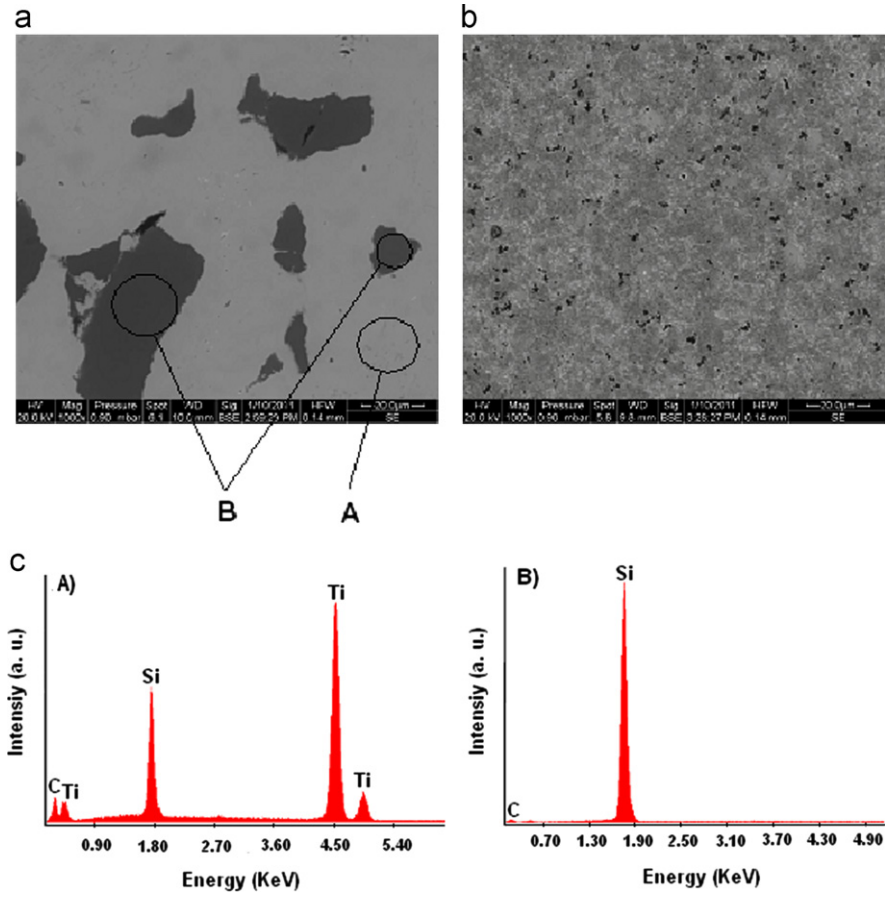

Fig. 5. SEM images of the spark plasma sintered (a) M1 sample, (b) M2 sample and (c) EDS of two different zones of the M1 sample.

state reaction [29], TiC was the main formed phase during mechanical alloying. The peaks broadening in the XRD pattern were the result of particles refinement and a possible amorphous phase formation.

After sintering the mechanically alloyed sample (M2), the XRD pattern (Fig. 3d) revealed that TiC and Ti_3SiC_2 were the major formed phases. $TiSi_2$ appeared as the minor phase with very low intensity peaks. This result was also observed by Zhang et al. [26].

Table 2
Atomic contents of Ti, Si and C in the selected A and B zones.

Zone	Element	Atomic (%)	Phase
A	Ti	49.84	Ti_3SiC_2
	Si	16.96	
	C	33.20	
B	Si	50.98	SiC
	C	49.02	

Table 3
The densities of the bulk materials.

Bulk material	Measured density	Theoretical density	Relative density (%)
M1	4.2762	4.450	96.09
M2	4.6127	4.679	98.58

Thus the previous mechanical alloying of the starting powders (sample M2), leads to the intermediate TiC and $TiSi_2$ formation which did not enhance the Ti_3SiC_2 purity through SPS in the same sintering conditions.

Table 1 gives the weight contents of the formed phases determined by the FullProf program based on the Rietveld method.

Fig. 4 gives an example of FullProf program fit of the XRD pattern of (a) the M1 and (b) the M2 samples after the SPS process.

Fig. 5 shows SEM micrographs, in BSE mode, of polished surface of the bulk materials obtained after the sintering of M1 and M2 samples. For the M1 bulk sample (Fig. 5a), the surface presents large pores with low density. Whereas, the M2 bulk sample of the powders mixture previously mechanically alloyed (Fig. 5b), presents rather a surface with large density of smaller pores homogeneously distributed.

The corresponding energy-dispersive X-ray spectra (EDX) of the A and B zones are shown in Fig. 5c. The A zone with bright field indicates a heavy phase composition, whereas the B zone with darker field points out a lighter phase composition. The chemical analysis results are listed in Table 2. These results are in a good agreement with the XRD patterns of Fig. 3b.

Table 3 shows the measured densities of M1 and M2 bulk materials. The measured densities were found to be respectively equal to 96.09% and 98.58% of theoretical for

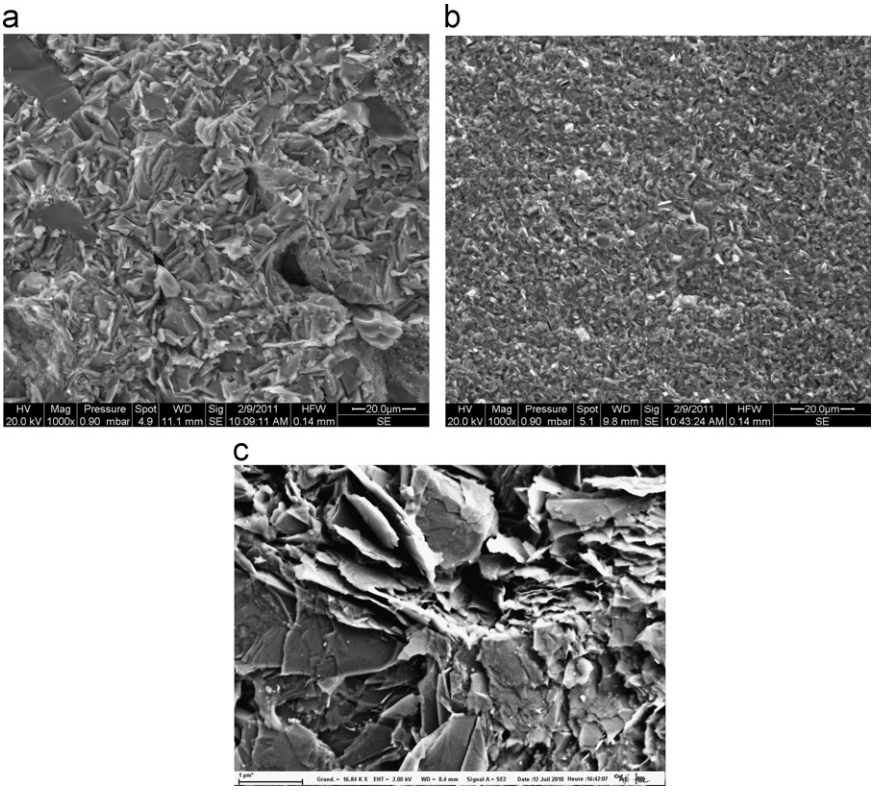

Fig. 6. SEM micrographs of the fracture surface of (a) M1, (b) M2 spark plasma sintered samples and (c) detail of M1 sample confirming the layered nature of Ti_3SiC_2.

M1 and M2 sintered samples. The theoretical density was calculated by considering the Ti_3SiC_2 purity in Table 1.

It could be concluded from these two values that the previous mechanical alloying of the powder is an effective way to improve the density of the sintered bulk material.

Fig. 6 shows the SEM micrographs of fractured surfaces of bulk samples prepared by spark plasma sintering of M1 and M2 powder mixtures. As observed in Fig. 6, the fracture mode is similar for all the bulk samples and is mostly intergranular. Cleavages with large flat and smooth surfaces can also be observed corresponding to transgranular grain fracture (Fig. 6a). The presence of these two fracture modes indicates the existence of phases with different hardness.

For the previously mechanically alloyed sample (M2), the fractured surface (Fig. 6b) consists of numerous smaller surface and cleavages as compared to the sintered M1 sample. This is due to the refining effect of the starting particles. Some closed pores can also be observed in the fractured surface of the M1 sample indicating that the bulk material did not reach its maximum densification. Fig. 6c shows a detail of an open pore of the M1 sample confirming the layered nature of Ti_3SiC_2 the ternary carbide.

The Vickers microhardness measured for both bulk samples M1 and M2 shows a significant improvement for the previously mechanically alloyed powders mixture, as it was of about 581.2 Hv (5.7 GPa) for M1 and 1282 Hv

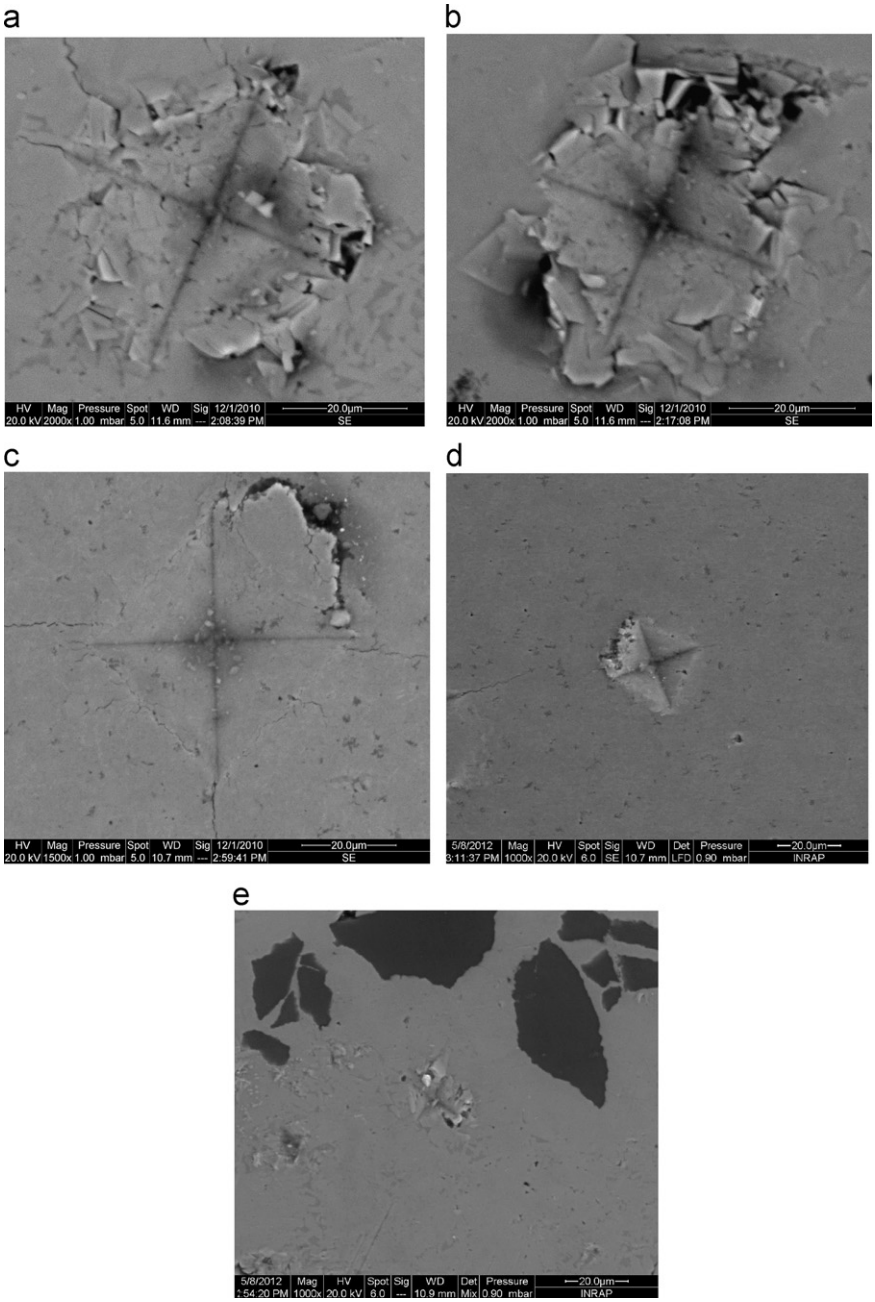

Fig. 7. SEM micrographs of the Vickers indentation marks for (a, b) M1 bulk sample under a charge of 5 N and (c, d) M2 bulk sample under a charge of 5 N and 1 N respectively, and (e) M1 bulk sample under a charge of 1 N.

(12.57 GPa) for M2. This microhardness increase for M2 is rather attributed to the important increase of the TiC content after sintering (about 51%) than to the decrease of porosity and the increase of the relative density from 96.04% to 98.58% after sintering. Lis et al. [30] while studying the microhardness of Ti_3SiC_2–TiC composites as a function of the TiC content estimated that for pure Ti_3SiC_2 a microhardness of 4 GPa should be obtained. Therefore the reported microhardness values in this work are in agreement with the results of [30] as the microhardness is lower for the sample M1 containing the highest content of Ti_3SiC_2 and the lesser content of TiC.

Fig. 7 shows the SEM micrographs of cracks induced by Vickers indentation for the bulk M1 and M2 samples. Fig. 7a and b shows a typical type of damage induced by Vickers indentation for Ti_3SiC_2 specimens. It is well known that indentations on ceramics often produce sink-in under the tip of the indentation. Conversely, in metals the material in surrounding area of the indentation often rises above the unindented surface level by plastic deformation. However, the damage observed in Fig. 7, cannot be related to classic behavior of either metals or ceramics. According to the microstructural observations of the damage around indentation in the Fig. 7, it is perceived that micro cracks developed along the surrounding grain boundary, leading to the intergranular cracking and grain separation. Very similar observations were obtained for the Vickers indentation marks on Ti_3SiC_2 elaborated by hot pressing Ti, SiC and C powders. The damage was found to be confined to the immediate vicinity of the indentations and the material in the surrounding area of the indentations was piled up as a result of a combination of grain push-out, pull-out, break-up and buckling [31].

However, the Fig. 7c and d, showing the cracks induced by Vickers indentation for the bulk M2 sample, reveal a less damaged indentation which indicates an apparent improvement of the microhardness even though the material in the vicinity of the indentation was still piled up. These results are in agreement with the microhardness values of the respective bulk samples (5.7 GPa for sintered M1 and 12.57 GPa for M2 sintered samples, respectively). On the other hand, the increase of the measured microhardness values at low loads (1 N) (822.28 Hv (8.064 GPa) and 1366 Hv (13.4 GPa) for respectively M1 and M2 sintered samples) and the nature of the damage observed surrounding the indentations (Fig. 7d and e) are assumed to be indications of the ability to Ti_3SiC_2 to display microscale plasticity [31].

Fig. 8 shows AFM images of the Vickers indentations marks of M1 and M2 bulk samples. It is clearly observed that for the sintered M1 sample, the surface surrounding the indentation mark was piled up (Fig. 8a and b) showing rather a soft material behavior. Whereas for M2 sintered sample a less damaged area around the indentation and more regular indentation mark profiles could be observed indicating a more harder bulk material (Fig. 8c and d).

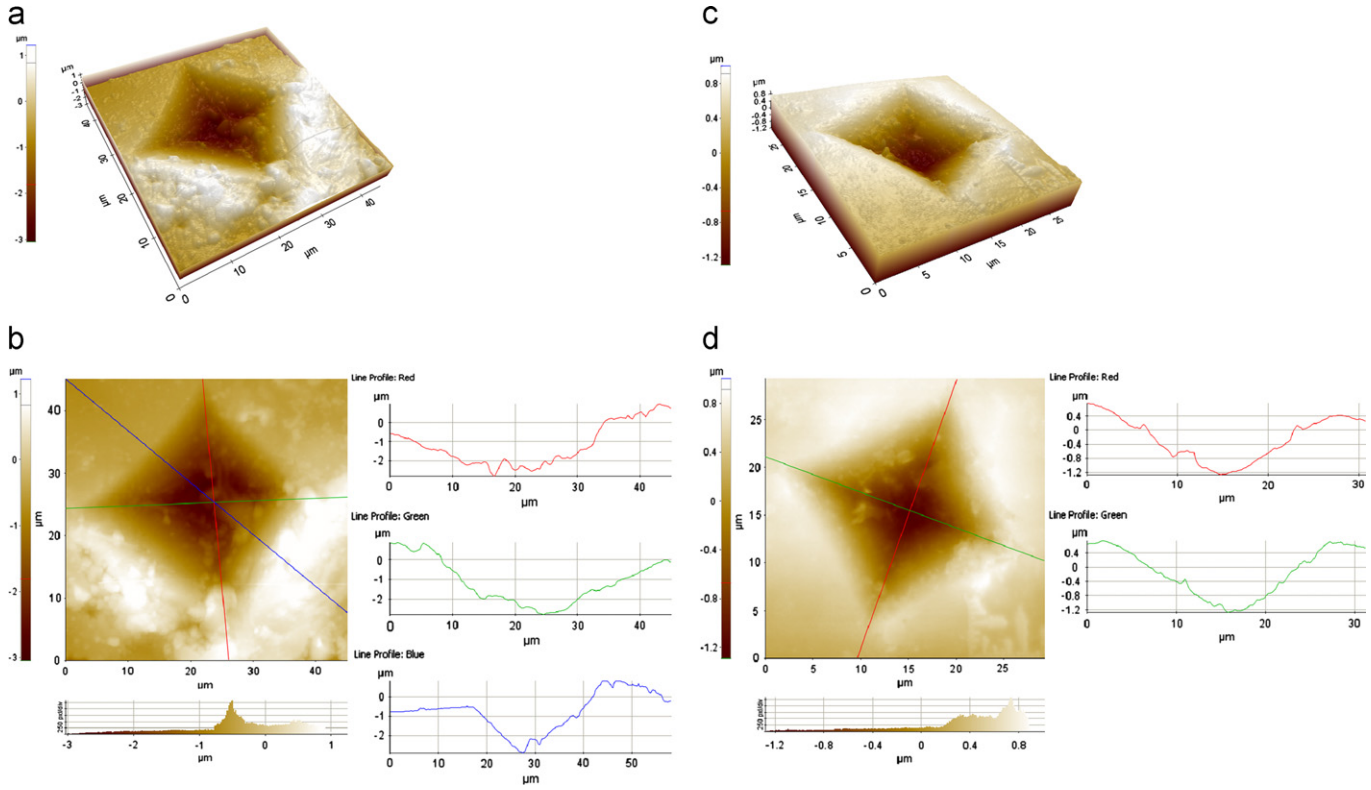

Fig. 8. AFM images of the Vickers indentations marks for (a, b) M1 bulk sample and (c and d) M2 bulk sample.

4. Conclusion

Simultaneous synthesis and densification of Ti_3SiC_2 was rapidly achieved by spark plama sintering of 5Ti/2SiC/C powder mixture. The previous mechanical alloying process of the starting powder mixture was investigated in order to study its effect on the Ti_3SiC_2 purity as well as the mechanical property of the formed bulk materials.

It was found that the mechanical alloying of the starting powder was not advantageous for Ti_3SiC_2 purity. Nevertheless, the relative density of the bulk materials was found to be improved to 98.58% for the sintered mechanically alloyed sample, whereas it was not more than 96.04% for the sintered Ti/SiC/C powder mixture. The cracks induced by the microhardness test showed that micro cracks nucleated along the surrounding grain boundary leading to the intergranular cracking and grain separation. On the other hand, it was found that the previous mechanical alloying has a good effect on microhardness of the bulk material by increasing the TiC contents.

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