Physico-chemical and mechanical properties of Ti_3SiC_2 -based materials elaborated from SiC/Ti by reactive spark plasma sintering

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Abstract: In this paper, the synthesis of Ti_3SiC_2 from SiC/Ti powder using reactive spark plasma sintering (R-SPS) in the temperature range of 1300–1400 °C is reported. The results show that the purity of Ti_3SiC_2 is improved up to 75 wt% when the holding time is increased from 10 to 20 min at 1400 °C. The thermodynamic and experimental results indicate that Ti_3SiC_2 formation takes place via the reaction of a pre-formed TiC phase with the silicides, formed from the eutectic compositions. Detailed analysis of mechanical behaviour indicates that samples with higher percentage of secondary phases exhibit higher microhardness and better resistance compared to the near single phase Ti_3SiC_2 .

Keywords: Ti_3SiC_2 ; reactive spark plasma sintering (R-SPS); density; mechanical properties.

1 Introduction

Titanium silicon carbide (Ti_3SiC_2) is a remarkable compound which has a special crystalline structure. It takes the form of a layered hexagonal structure, in which almost close-packed planes of titanium are separated from each other by hexagonal nets of silicon, whereas carbon atoms occupy the octahedral sites between the titanium layers [1,2]. This particular structure allows the ternary carbide of Ti_3SiC_2 to combine the best properties of both ceramics and metals [3,4]. Indeed, it has low density (4.53 g/cm³), good thermal and electrical conductivity, and high thermal stability.

Nowadays, many mixtures of starting materials are used to prepare the ternary carbide compound. In this context, our group has used several starting mixtures to elaborate Ti_3SiC_2 . Among these mixtures, we quote Ti/Si/C [5], Ti/C/SiC [6], Ti/SiC [7], and Si/TiC [8]. Several researchers reported on the synthesis of Ti_3SiC_2 starting from Ti/SiC in fine powder or non-powder forms such as films, foils, and rods by using different processes [9–14]. These sintering processes were often performed at relatively high temperature (more than 1400 °C) for a long time. However, in our recent article [7], to elaborate the ternary carbide from Ti/SiC, we have used an innovative technique for rapid sintering, i.e., spark plasma sintering (SPS).

Many investigations have shown that various SPS parameters play a crucial role in the *in situ* synthesis of bulk materials during spark plasma sintering [15–17].

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It has been shown that the reactivity and formation of different phases have been enhanced. In this context, SPS is considered to be a powerful technique for the simultaneous synthesis and consolidation of Ti_3SiC_2 . Several researchers have succeeded in synthesis of Ti_3SiC_2 producing high purity [18–20] but that does not prevent it being consistently accompanied with the secondary phases. Indeed, TiC, SiC or Ti_5Si_3 and TiSi_2 phases appear inevitably after sintering whatever the starting powder mixture used. Several studies [21,22] have revealed that the purity of Ti_3SiC_2 as well as the corresponding bulk material properties are intimately related to the spark plasma sintering parameters.

The present work is a continuation of our previous studies [5–8]. The main purpose of this work is to study the influence of the grain size of the starting mixture by using the same starting mixture Ti/SiC as in our previous work [7], but which differs by the micro-structure of silicon carbide. In our previous study, the SiC was in the form of nano-particles with 5 nm in size while in the present work micro-meter powder (44 μm) was used. This will lead to a significant difference in the nature as well as the amount of the obtained phase. Furthermore, the influence of various SPS parameters, such as temperature and holding time, on Ti_3SiC_2 formation will be studied.

2 Experimental

Starting powders of Ti (< 40 μm , 98%, Prolabo) and SiC (44 μm , 99%, Alfa Aesar) were used in this study. The SiC powder used is polycrystalline and contains traces of free C. The starting powders were uniformly mixed in a GFL 3040 shaker mill for 48 h to ensure better homogenization. The molar ratio of Ti–SiC was adjusted to 3:2. In order to obtain a pure Ti_3SiC_2 phase, non-stoichiometric proportions of SiC have been used in order to have an excess of Si. Indeed, the silicon has a relatively low melting temperature (1414 °C [23]) compared to titanium, and it presents the risk of loss by evaporation during the sintering process. Thus, the formation of relatively large quantities of Ti_3SiC_2 likely occurs in parallel with the evaporation of some amounts of Si(g).

The bulk sample was processed by the spark plasma sintering (SPS) route using a Syntex society model 515S apparatus. After establishing a secondary vacuum and passing an argon flow into the apparatus, a uniaxial

pressure and a high-pulsed DC current were applied to the cylindrical graphite die containing the powder placed between two electrodes. The sintering temperatures were monitored through an infrared camera (pyrometer CHINO IR-AH S2) and were controlled in the range of 1300–1400 °C at a heating rate of 60 °C/min. The holding time was varied from 10 to 20 min. The applied pressure was maintained constant at 60 MPa. Sintered samples exhibited, respectively, a thickness and a diameter of 4 mm and 8 mm. The sintering temperature, the axial pressure, and the ram displacement were recorded according to the time taken to monitor the compaction powder compacted during the sintering process.

X-ray diffraction (XRD) using Cu K α radiation was performed to identify the phases that were present in the starting powder as well as the bulk samples. The proportions of formed phases were determined by the FullProf program [24] using the Rietveld method [25].

Thermal stability of the starting powder was performed by differential thermal analysis (DTA) using a SETARAM-Setsys Evolution 16, a thermal analysis instrument, with a heating rate of 10 K/min under Ar flow.

The morphology of each synthesized bulk material was carried out using a Zeiss Supra 40 VP field emission gun scanning electron microscope (FEG-SEM).

The micro-analysis of each synthesized sample was carried out using the FEI Quanta 200 environmental scanning electron microscope coupled with EDX micro-analyzer.

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

The micro-hardness measurements were conducted on the pellets' plane using a Duramin 20 Vickers device under a test force of 1 N for 7 s. Each reported Vickers hardness value represents the average of ten measurements. The images of the damage induced by the Vickers indentation marks were recorded using the Park Systems XE-70 atomic force microscope while adopting the noncontact mode.

The compressive tests of parallelepiped specimens with dimensions of 2 mm $\times$ 2 mm $\times$ 3 mm were carried out using a Deben 5KN tensile compression stage with an extension rate of 0.5 mm/min.

The nano-indentation measurements were performed

using an MTS nano-indenter XP equipped with a diamond tip of Berkovich type. The parameters fixed for the measures were: an imposed depth of 2000 nm, a deformation speed of 0.05 s^{-1} , and a frequency of 45 Hz.

3 Results and discussion

3.1 DTA analysis

In order to better specify the temperature range at which the ternary carbide sintering would take place, we had recourse to differential thermal analysis (DTA). This technique allowed us to determine the temperature and type of all thermal changes (endothermic or exothermic). Figure 1 portrays the DTA thermogram of the starting powder mixture of Ti/SiC. The curve shows a weak broad endothermic peak starting at about 890°C and another intense sharp exothermic one peak at 1340°C . The occurrence of the large endothermic peak was not due to the formation of Ti_5Si_3 and TiC because this process generated substantial heat [26]. It can be seen from the Ti–Si binary phase diagram [27] that the phase transition from α -Ti to β -Ti began at about 882°C . This phase transition was an endothermic process because the thermal capacity of β -Ti was greater than that of α -Ti [28]. So, the endothermic peak was likely derived from this phase transition.

Besides, the intense exothermic peak at 1340°C indicated that there was a strong phase forming reaction that took place: this can be due to the formation of the Ti_3SiC_2 phase. This result was also observed by Kuang *et al.* [12]. Another study conducted by Sato *et al.* [26] revealed that TiC and Ti_5Si_3 were

the major formed phases in the temperature range 1000 – 1300°C . They asserted that the Ti_5Si_3 phase disappeared for higher temperature whereas the Ti_3SiC_2 phase started to appear above 1300°C .

In order to determine whether these DTA peaks were accompanied by any phase change, XRD analysis was performed. The results of XRD analysis at 890°C after DTA analysis show that only α -Ti and SiC could be detected and no formation of a new phase occurred. It should be noted that α -Ti is observed instead of β -Ti since this phase transition is reversible. However, at 1340°C , the formation of the new phase Ti_3SiC_2 occurred. Other phases are present such as TiSi_2 and SiC in small quantities. Thus we can conclude that the best sintering temperature lies in the 1300 – 1400°C range.

3.2 Reactive SPS process

Reactive SPS process is carried out thanks to two main factors: the application of pressure and temperature rise by the Joule effect. All the displacement profiles during the SPS process of the $3\text{Ti}/2\text{SiC}$ powder recorded according to pressure and temperature were similar. As an example, Fig. 2 shows a typical punch displacement recorded during the SPS process of $3\text{Ti}/2\text{SiC}$ powder mixture sintered at 1400°C for 20 min under 60 MPa. The SPS process was conducted as follows: the pressure was increased to 60 MPa for 1 min and then kept constant during the compaction cycle. As for the temperature, it was maintained at a value close to 600°C for 6 min and then increased to 1400°C and held constant for 20 min. During the first 7 min, the strong shrinkage caused by the increase in pressure in the vacuum chamber corresponds to a degassing phenomenon that is probably due to vaporization of species adsorbed on the particle surface. The first recess (1.7 mm) corresponds rather to the compaction of the powder. As in previous works [5–8], this displacement is probably attributed to the re-arrangement of the initial powder particles under the sole effect of the applied pressure since the temperature is still too low to induce any phase transformation. Between 600 and 1060°C , the displacement increases to 2.6 mm under the combined effect of temperature and pressure. At this stage, phase formations are observed, such as silicides TiSi_2 and Ti_5Si_3 as well as carbide TiC , accompanied by softening of the particle surface. At $\Delta t = 17$ min, the pressure being maintained at a maximum of 60 MPa,

Fig. 1 DTA curve of the powder mixture of Ti and SiC.

Fig. 2 Variation of sintering temperature, sample shrinkage, and applied pressure during the SPS process for Ti/SiC powder mixture heated at 1400 °C for 20 min. Left y-axis corresponds to the sintering temperature and right y-axis corresponds to sample shrinkage.

the displacement abruptly increases to a value of 3.1 mm when the temperature reaches 1250 °C. We assume that this displacement is related to a phase transformation from a less dense to a denser material. Then, the displacement increased progressively to 3.4 mm as the temperature reached its maximum of 1400 °C. This displacement can be attributed to the densification of the new formed phases. In the cooling stage from 1400 to 600 °C, the displacement increase is due to thermal shrinkage, when the current is switched off and the temperature falls.

In order to investigate the effect of sintering temperature and holding time on the formation of Ti_3SiC_2 , we plotted the variation of the piston displacement during sintering of mixtures versus time at 1300, 1350, and 1400 °C for 10 min (Fig. 3(a)) and at 1300 °C for 10, 15, and 20 min (Fig. 3(b)). Figure 3(a) shows that, at the stage “temperature rise”, the piston displacement is greater at a higher temperature, which favours the Ti_3SiC_2 formation. However, from Fig. 3(b), the piston displacement varies only slightly by prolonging the holding time by 10 to 20 min. This leads us to conclude that Ti_3SiC_2 formation is attributed to the sintering temperature rather than the holding time.

3.3 X-ray characterizations

Figure 4 displays the X-ray diffraction (XRD) patterns of the 3Ti/2SiC powder mixture and the bulk materials obtained after SPS for different holding time (10, 15, and 20 min) in the 1300–1400 °C temperature range.

Fig. 3 Variation of the piston displacement during sintering of mixtures versus time: (a) at 1300, 1350, and 1400 °C for 10 min and (b) at 1300 °C for 10, 15, and 20 min.

After sintering the 3Ti/2SiC powder mixture, it was found that all the Ti peaks disappeared in the XRD patterns and that only the peaks of the starting SiC phase with low intensity could be detected, compared to the initial mixture. It should also be noted that new phases such as Ti_3SiC_2 , TiC, Ti_5Si_3 , and TiSi_2 were formed (Fig. 4(a)). Moreover, when the sintering temperature was increased from 1300 to 1350 °C, it was observed that the intensities of TiC and Ti_5Si_3 peaks decreased noticeably (Fig. 4(b)) and then disappeared completely at 1400 °C (Fig. 4(c)). However, TiSi_2 peaks appeared at 1300 °C for 20 min and increased in intensity when the temperature increased (Figs. 4(b) and 4(c)). Regardless of the temperature and the holding time, Ti_3SiC_2 was practically the main formed phase particularly for a sintering temperature as high as 1400 °C (Fig. 4(c)). This result was previously observed by Gottselig *et al.* [10].

Fig. 4 XRD profiles of 3Ti/2SiC powder and samples sintered for different holding time (10, 15, and 20 min) in the studied temperature range of 1300–1400 °C.

The observed intense peak of carbon was probably related to the graphite foil used in order to prevent the powder from reacting with the surface of the graphite die and the graphite punches.

To explain the Ti_3SiC_2 formation from Ti/SiC powder, Kuang *et al.* [12] proposed the following mechanism using hot pressing technique. The authors assumed that firstly, SiC reacted with Ti at the interface which resulted in the formation of TiC and Si. Then, some of the released Si reacted with Ti to form TiSi_2 and Ti_5Si_3 . Finally, these titanium silicides would react with TiC to form the ternary carbide Ti_3SiC_2 .

For the Ti_3SiC_2 formation by SPS from the Ti/SiC mixture, we have adopted the same mechanism proposed in our previous work [7]. We proposed that TiC phase would probably be formed initially from Ti and SiC. Indeed, thermodynamically, this reaction is more favourable among all the other possible reactions.

Then, presumably, a eutectic liquid could be formed at 1330 °C from the released Si and Ti. The two phases TiSi_2 and Ti_5Si_3 will be formed from the two eutectic compositions Si– TiSi_2 and Ti– Ti_5Si_3 [14]. Finally, these silicides would react with the TiC formed to give the ternary carbide Ti_3SiC_2 .

In summary, based on the results of the DTA and XRD analyses, three temperature ranges have been established with respect to the phases formed:

(1) 600–900 °C:

The phase transition from α -Ti to β -Ti began at about 882 °C

(2) 900–1330 °C:

Formation of TiC in direct contact with SiC and β -Ti

Formation of a eutectic mixture of Si– TiSi_2 and Ti– Ti_5Si_3 composition at 1330 °C, which allows faster diffusion which increases the reactivity of the system

(3) 1340–1450 °C:

Formation predominantly of Ti_3SiC_2 according to the following reaction

3.4 FEG-SEM characterizations

Figures 5(a)–5(c) illustrate the FEG-SEM micrographs in back-scattering electrons (BSE) mode of the bulk materials' polished surface obtained after 20 min of sintering at respectively 1300, 1350, and 1400 °C. All the samples have a similar surface aspect with distinct phases. The difference between the surface of

Fig. 5 FEG-SEM micrographs of the polished surface of bulk materials obtained after sintering for 20 min at (a) 1300, (b) 1350, and (c) 1400 °C.

the different samples sintered at increasing temperatures can be related to the number of dark grey regions which decreased by increasing the temperature. For all samples, the dark grey regions represent lighter phases and the clear regions are the heaviest.

These results were confirmed by energy dispersive X-ray analysis (EDX) and element mapping of the bulk material obtained after 20 min of sintering at 1400 °C (Fig. 6). The element mapping only gives a qualitative image of the distribution of Si (Fig. 6(b)) and Ti (Fig. 6(c)) of the sample. The corresponding energy-dispersive X-ray spectra of two different zones A and B are shown in Figs. 6(d) and 6(e), respectively. The darker zone (A) corresponds to a lighter phase, where its chemical composition (Fig. 6(d)) is similar to the SiC phase. However, the bright zone (B) is indicative of a heavy phase. Its chemical composition (Fig. 6(e)) matches a mixture of Ti_3SiC_2 and TiSi_2 .

Fig. 6 (a) EDX micrograph of the bulk material obtained after sintering at 1400 °C for 20 min, (b) Si mapping, (c) Ti mapping, (d) the A zone, and (e) the B zone.

These results are in good agreement with the XRD patterns of Fig. 4(c).

3.5 Rietveld refinement results

In order to determine the content of each phase obtained after sintering, we used the Fullprof program, based on the Rietveld method. Figure 7 presents an example of a Fullprof program fit of the XRD pattern of the sample sintered at 1400 °C for 20 min. The observed pattern is denoted by a red dot, whereas the

Fig. 7 Example of Fullprof program fit of Ti/SiC sample after SPS sintering at 1400 °C for 20 min ($\chi^2 = 3.8$).

Calculated pattern is denoted by a black line and the difference curve is given at the bottom of the plot by a blue line. As we see in Table 1, the refinement quality factors (R_{wp} , R_B , and R_F) are satisfactory.

The Rietveld refinement confirmed that the main-phase Ti₃SiC₂ crystallizes in a hexagonal structure with a $P6_3/mmc$ space group and the calculated lattice parameters are $a = 3.06861(3)$ Å and $c = 17.67923(1)$ Å. These calculated values of lattice parameters are very close to those given in the JCPDS reference pattern 01-074-0310 ($a = 3.0680$ Å and $c = 17.6690$ Å). It could be seen that there was no considerable change in the lattice parameters with the sintering temperature.

The composition stoichiometry of the phases was determined by the Rietveld refinement and the weight contents of the formed phases are reported in Table 1.

From Table 1, it can be concluded that when Ti/SiC was sintered at 1300 °C for 10 min, the weight content of Ti₃SiC₂ reached about 26%. However, the major formed phase of Ti₅Si₃ exceeded 40%. By prolonging the sintering time from 10 to 20 min, while keeping the same temperature (1300 °C), Ti₃SiC₂ formation was favoured at the expense of other phases present. Thus, it can be deduced that Ti₃SiC₂ is formed by the dissolution of the phases present in the reaction medium (Ti₅Si₃, TiC, and SiC).

Table 1 Rietveld refinement results of the bulk materials sintered at 60 MPa by SPS starting from mixture of Ti–SiC

SPS conditions	Rietveld refinement results	Ti ₃ SiC ₂ (<i>P6₃/mmc</i>)	SiC (<i>P6₃mc</i>)	TiC (<i>Fm$\bar{3}$m</i>)	Ti ₅ Si ₃ (<i>P6₃/mcm</i>)	TiSi ₂ (<i>Fddd</i>)	C (<i>P6₃/mmc</i>)	χ^2
1300 °C- 10 min	Lattice parameters (Å)	<i>a</i> = 3.06928(5) <i>c</i> = 17.67974(6)	<i>a</i> = 3.08116(4) <i>c</i> = 15.10260(1)	<i>a</i> = 4.31960(8)	<i>a</i> = 7.44799(9) <i>c</i> = 5.16885(1)	—	<i>a</i> = 2.46839(6) <i>c</i> = 6.70829(8)	7.14
	Lattice volume (Å ³)	144.234	124.165	80.599	248.197	—	35.396	
	Weight contents (%)	25.58 (0.26)	20.09 (0.27)	13.46 (0.20)	40.44 (0.31)	—	0.43 (0.01)	
	< <i>D</i> > (nm)	67	66	87	82	—	24	
	<i>R_B</i>	5.31	8.41	4.27	7.94	—	3.39	
	<i>R_F</i>	5.19	6.32	2.43	5.60	—	5.48	
1300 °C- 15 min	Lattice parameters (Å)	<i>a</i> = 3.067925(6) <i>c</i> = 17.67971(4)	<i>a</i> = 3.08075(2) <i>c</i> = 15.10631(5)	<i>a</i> = 4.31917(6)	<i>a</i> = 7.44742(2) <i>c</i> = 5.14759(3)	—	<i>a</i> = 2.46444(5) <i>c</i> = 6.70813(4)	6.76
	Lattice volume (Å ³)	144.106	124.162	80.575	247.286	—	35.282	
	Weight contents (%)	41.77 (0.28)	16.28 (0.25)	5.28 (0.17)	36.52 (0.29)	—	0.16 (0.01)	
	< <i>D</i> > (nm)	70	69	90	84	—	25	
	<i>R_B</i>	5.87	8.54	2.10	8.46	—	7.47	
	<i>R_F</i>	4.57	7.63	1.15	4.52	—	6.00	
1300 °C- 20 min	Lattice parameters (Å)	<i>a</i> = 3.06921(5) <i>c</i> = 17.67963(5)	<i>a</i> = 3.08064(8) <i>c</i> = 15.10175(7)	<i>a</i> = 4.31912(4)	<i>a</i> = 7.44633(5) <i>c</i> = 5.14658(4)	<i>a</i> = 8.26894(8) <i>b</i> = 4.80623(9) <i>c</i> = 8.55574(6)	<i>a</i> = 2.46347(2) <i>c</i> = 6.70820(9)	6.21
	Lattice volume (Å ³)	144.226	124.116	80.572	247.200	340.026	35.255	
	Weight contents (%)	54.78 (0.28)	10.83 (0.26)	1.33 (0.08)	28.57 (0.27)	4.26 (0.12)	0.24 (0.01)	
	< <i>D</i> > (nm)	76	71	94	87	35	28	
	<i>R_B</i>	6.00	8.47	3.02	4.21	7.90	3.88	
	<i>R_F</i>	4.53	7.35	2.45	3.74	6.15	4.98	
1350 °C- 10 min	Lattice parameters (Å)	<i>a</i> = 3.06917(6) <i>c</i> = 17.67945(7)	<i>a</i> = 3.08062(4) <i>c</i> = 15.09876(3)	<i>a</i> = 4.31908(3)	<i>a</i> = 7.44629(3) <i>c</i> = 5.14655(6)	—	<i>a</i> = 2.46342(3) <i>c</i> = 6.70685(4)	7.07
	Lattice volume (Å ³)	144.221	124.090	80.570	247.123	—	35.246	
	Weight contents (%)	47.13 (0.34)	13.79 (0.23)	2.83 (0.11)	35.59 (0.25)	—	0.66 (0.01)	
	< <i>D</i> > (nm)	73	74	97	89	—	29	
	<i>R_B</i>	5.74	8.19	3.01	5.64	—	3.46	
	<i>R_F</i>	3.97	7.94	2.34	6.24	—	9.28	
1350 °C- 15 min	Lattice parameters (Å)	<i>a</i> = 3.06873(3) <i>c</i> = 17.67936(2)	<i>a</i> = 3.08054(1) <i>c</i> = 15.09305(2)	—	<i>a</i> = 7.44628(5) <i>c</i> = 5.14657(8)	<i>a</i> = 8.26712(6) <i>b</i> = 4.80745(7) <i>c</i> = 8.55565(2)	<i>a</i> = 2.46333(2) <i>c</i> = 6.70603(4)	7.42
	Lattice volume (Å ³)	144.179	124.036	—	247.124	340.034	35.239	
	Weight contents (%)	53.08 (0.31)	11.39 (0.19)	—	30.96 (0.26)	4.04 (0.15)	0.53 (0.01)	
	< <i>D</i> > (nm)	74	79	—	93	39	32	
	<i>R_B</i>	5.83	10.2	—	5.21	8.15	5.15	
	<i>R_F</i>	4.37	8.51	—	7.11	7.16	5.10	
1350 °C- 20 min	Lattice parameters (Å)	<i>a</i> = 3.06861(3) <i>c</i> = 17.67923(1)	<i>a</i> = 3.08044(5) <i>c</i> = 15.09265(4)	—	<i>a</i> = 7.44626(6) <i>c</i> = 5.14652(4)	<i>a</i> = 8.26593(6) <i>b</i> = 4.80563(4) <i>c</i> = 8.55476(4)	<i>a</i> = 2.46296(7) <i>c</i> = 6.70566(3)	6.54
	Lattice volume (Å ³)	144.166	124.025	—	247.120	339.821	35.227	
	Weight contents (%)	58.37 (0.31)	11.30 (0.21)	—	16.62 (0.22)	12.86 (0.17)	0.54 (0.01)	
	< <i>D</i> > (nm)	83	84	—	96	44	34	
	<i>R_B</i>	5.54	10.30	—	6.23	10.40	2.90	
	<i>R_F</i>	4.23	9.01	—	4.75	7.49	10.60	
1400 °C- 10 min	Lattice parameters (Å)	<i>a</i> = 3.06857(6) <i>c</i> = 17.67915(3)	<i>a</i> = 3.08032(1) <i>c</i> = 15.09169(3)	—	—	<i>a</i> = 8.26465(4) <i>b</i> = 4.80383(4) <i>c</i> = 8.55399(7)	<i>a</i> = 2.46278(7) <i>c</i> = 6.70546(3)	3.08
	Lattice volume (Å ³)	144.162	124.232	—	—	339.610	35.221	
	Weight contents (%)	71.96 (0.38)	8.92 (0.25)	—	—	18.38 (0.19)	0.74 (0.01)	
	< <i>D</i> > (nm)	76	89	—	—	46	36	
	<i>R_B</i>	5.30	7.53	—	—	4.50	2.90	
	<i>R_F</i>	3.36	6.01	—	—	3.91	10.60	

Continued 1

SPS conditions	Rietveld refinement results	Ti ₃ SiC ₂ (P6 ₃ /mmc)	SiC (P6 ₃ mc)	TiC (Fm $\bar{3}$ m)	Ti ₅ Si ₃ (P6 ₃ /mcm)	TiSi ₂ (Fddd)	C (P6 ₃ /mmc)	χ^2
1400 °C - 15 min	Lattice parameters (Å)	$a = 3.06849(6)$ $c = 17.67899(2)$	$a = 3.08025(4)$ $c = 15.09157(2)$	—	—	$a = 8.26425(4)$ $b = 4.80339(3)$ $c = 8.55309(4)$	$a = 2.46256(7)$ $c = 6.70521(3)$	4.36
	Lattice volume (Å ³)	144.153	124.280	—	—	339.527	35.213	
	Weight contents (%)	72.97 (0.42)	11.01 (0.26)	—	—	15.31 (0.18)	0.71 (0.01)	
	<D> (nm)	80	98	—	—	49	38	
	R _B	4.92	11.3	—	—	5.75	2.90	
	R _F	3.11	7.61	—	—	4.85	10.60	
1400 °C - 20 min	Lattice parameters (Å)	$a = 3.06845(2)$ $c = 17.67833(4)$	$a = 3.08021(7)$ $c = 15.09152(9)$	—	—	$a = 8.26364(3)$ $b = 4.80331(4)$ $c = 8.55289(3)$	$a = 2.46248(7)$ $c = 6.70514(3)$	3.81
	Lattice volume (Å ³)	144.144	124.250	—	—	339.488	35.210	
	Weight content (%)	74.57 (0.44)	13.20 (0.27)	—	—	11.50 (0.18)	0.72 (0.01)	
	<D> (nm)	84	103	—	—	52	41	
	R _B	5.67	5.21	—	—	6.08	2.90	
	R _F	4.22	6.11	—	—	4.77	10.60	

By increasing the sintering temperature from 1300 to 1350 °C, we continued to promote Ti₃SiC₂ formation with the appearance of the new phase of TiSi₂ in the medium. At 1400 °C, the total disappearance of Ti₅Si₃ and TiC phases was noticed. Therefore, it can be concluded that these two phases were intermediate in the process of Ti₃SiC₂ formation from Ti/SiC powder. However, keeping the temperature at 1400 °C and extending the sintering time, it was found that TiSi₂ was dissolved in favour of Ti₃SiC₂ and SiC. Thus, for the sample sintered at 1400 °C for 20 min, the weight percentage of Ti₃SiC₂ reached about 75%. From the results obtained above, it can be deduced that the increase in temperature and sintering time promotes Ti₃SiC₂ formation from Ti/SiC powder.

A recent study, using titanium foils and polymer films highly filled with micro-sized SiC as starting materials [13], showed that the composition's result was quite close to our obtained material at a sintering temperature of 1400 °C. The material was synthesized by SHS process and consisted of 72, 14, and 13 wt% of Ti₃SiC₂, SiC, and TiSi₂, respectively, as well as traces of TiC and Ti₅Si₃C_x.

By comparison, the material elaborated in our previous work [7], underwent the same sintering conditions (1400 °C - 20 min), but it was synthesized from SiC of nano-metric size prepared by mechanical alloying. The obtained bulk material consisted of 61, 21, 11, 5, and 2 wt% of Ti₃SiC₂, TiC, Ti₅Si₃, TiSi₂, and SiC, respectively. However, for the present work, when

starting from micro-metric SiC, the elaborated bulk material contains a significantly higher Ti₃SiC₂ content (75%) and secondary phases are fewer (TiSi₂ and SiC).

We think that the difference is due to high chemical reactivity of nano-metric SiC (5 nm) which reacts easily with Ti to form a high concentration of TiC. This TiC phase is thermodynamically very stable and prevents the formation of a great proportion of Ti₃SiC₂.

However, SiC with greater diameter in the micro-meter range, reacts partly with Ti giving a significantly lower amount of TiC in comparison with nano-metric SiC. The sintering conditions applied (1400 °C, 60 MPa, 20 min), are sufficient to transform totally the as-formed TiC to Ti₃SiC₂, which is not the case when TiC formed in large quantities [7].

The average size of Ti₃SiC₂ coherence domains was calculated from Rietveld refinement. It is noticed, from Table 1, a considerable increase in the Ti₃SiC₂ crystallite size by increasing the sintering temperature or the holding time. We well noted the influence of temperature on the crystallite size; the diffusion becomes highest thereby increasing the particles' growth. Indeed, the size becomes larger for higher temperatures. As an example, for a holding time of 10 min, the size rises from ~67 nm at 1300 °C to ~76 nm at 1400 °C. As a comparison between present work and previous work [7], the evolution of Ti₃SiC₂ crystallite size as function of the sintering temperature (Fig. 8(a)) and the holding time (Fig. 8(b)) was illustrated. For both mixtures, a remarkable influence

Fig. 8 Evolution of the Ti_3SiC_2 crystallite size, for present work and previous work [7], as function of (a) sintering temperature and (b) holding time.

of the sintering conditions on the size of the crystallites was noted. Thus, an increase in temperature or an extension of the sintering time induces a progressive increase in the crystallite size. However, this crystallite growth during consolidation was limited and was the result of applying the SPS method. The materials elaborated in the previous work [7] have the lowest crystallite size values of Ti_3SiC_2 . This seems reasonable since we start from SiC of nano-metric size.

3.6 Density measurement

Table 2 recapitulates the SPS process conditions and the corresponding values of densities. The relative densities of the as obtained bulk materials were determined from both theoretical and measured densities. The theoretical densities were calculated taking into consideration the overall weight contents of the present phases in the obtained bulk material and their lattice volume calculated by taking into account the lattice parameters resulting from Rietveld refinement of XRD patterns. The results revealed that the relative

Table 2 Experimental conditions adopted during the SPS process and the corresponding values of densities (where T indicates sintering temperature; t soaking time, ρ_{mes} measured density of the compacted sample, ρ_{th} corresponding theoretical density, d_{rel} corresponding relative density)

T (°C)	t (min)	ρ_{mes} (g·cm ⁻³)	ρ_{th} (g·cm ⁻³)	d_{rel} (%)
1300	10	4.12	4.17	98.80
	15	4.15	4.20	98.84
	20	4.28	4.32	99.13
1350	10	4.20	4.25	98.87
	15	4.22	4.27	98.91
	20	4.35	4.36	99.77
1400	10	4.26	4.31	98.84
	15	4.26	4.29	99.30
	20	4.27	4.28	99.81

densities of the totality of obtained bulk materials were higher than 98%. However, regardless of the sintering temperature, the relative density increased with the increase of the holding time and became, for instance, higher than 99.9% for 20 min of holding time under a pressure of 60 MPa. According to the study of Istomin *et al.* [13], the relative density of the material synthesized by SHS process, subjected to vacuum heat-treatment under a mechanical load 0.2 MPa, does not exceed 80%, whereas with the SPS technique, a high density close to the theoretical density, can often be achieved.

The relationship between relative density of the material and the crystallite size of Ti_3SiC_2 is represented by Fig. 9. It is noticed that the relative density increases with an increase in the sintering temperature. Moreover, it is noted that a material is denser when the crystallite size is greater. Indeed, for the same temperature, the

Fig. 9 Crystallite size of Ti_3SiC_2 vs. relative density obtained from the samples sintered under 60 MPa for 10, 15, and 20 min at 1300, 1350, and 1400 °C.

relative density increases as the crystallite size grows and this is related to the low density of large pores.

3.7 Mechanical properties of bulk samples

Figure 10(a) shows the variation of the bulk materials' Vickers hardness as a function of holding time at different sintering temperatures. This figure displays that the Vickers hardness of the sintered samples decreased with the increase in the temperature and the holding time. The maximum experimental Vickers micro-hardness was about 10.5 ± 0.4 GPa (1077.12 Hv). This highest value was related to the highest weight contents of titanium silicide, titanium carbide, and silicon carbide in the corresponding bulk material sintered at 1300°C for 10 min. In fact, Ti_3SiC_2 tends to be a soft material and its hardness is as low as 4 GPa [3]. Whereas TiC, SiC, Ti_5Si_3 , and TiSi_2 have much higher hardness of about 28–35 GPa [29], 25 GPa [30], 11.65 GPa [31], and 8–10 GPa [32], respectively. The lowest measured hardness value that was close to 5 GPa (507.5 Hv), corresponded to the bulk material

obtained after 20 min of sintering at 1400°C , and this was attributed to the high weight content of Ti_3SiC_2 in the corresponding sample. We can estimate the Ti_3SiC_2 weight content for a hardness of 4 GPa using mathematical extrapolation. Thus, the bulk material should have about 85% of Ti_3SiC_2 weight content. These values are close to those extrapolated by Lis *et al.* [33]. A hardness of 2.5 GPa was obtained by extrapolation to a pure Ti_3SiC_2 (100 wt%). By referring to the work of Pampuch and Lis [34], a hardness of 2 GPa was measured in the case of single-phase Ti_3SiC_2 material prepared by pressureless sintering.

Figure 11 reveals the AFM images of the Vickers indentation marks of the bulk samples sintered for 10 min at 1300°C and for 20 min at 1400°C , respectively. It is clearly observed that the surface of the sample sintered at 1300°C (Figs. 11(a) and 11(b)) presents profiles with rather regular indentation indicating a harder bulk material. Whereas the surface surrounding the indentation mark of the sample sintered at 1400°C is piled up (Figs. 11(c) and 11(d)), showing a quite soft material behaviour.

Figure 12 shows the variation of the true stress as function of true strain for samples sintered for 20 min at 1300, 1350, and 1400°C . The compressive yield strength of the Ti_3SiC_2 specimens increased from 1040 to 1160 MPa with increasing sintering temperature. It could be seen that for all Ti_3SiC_2 specimens, the stress–strain curve was near to linearity indicating elastic deformation behaviour. It was remarkable to note that all samples sintered over the temperature range of 1300 – 1400°C displayed abrupt brittle fracture behaviour with no macro-plastic deformation being observed. Thus, it could be clearly shown that polycrystalline Ti_3SiC_2 bulk materials exhibit good resistance to damage during compressive tests. The above phenomena suggested that Ti_3SiC_2 is a damage tolerant material, undergoing micro-scale deformation during compressive testing [35]. Zhang and Sun [19] investigated the compressive behaviour of Ti_3SiC_2 with high purity ($\sim 99\%$) and reported the sample yielded at 935 MPa and deformation occurred by the formation of classic shear bands. This value of compressive yield strength is lower than those obtained for our material (1160 MPa). The difference between these values is probably due to presence of secondary phases SiC and TiSi_2 .

To understand the mechanisms of micro-scale deformation in polycrystalline Ti_3SiC_2 , the cracking

Fig. 10 Variation of the Vickers micro-hardness of sintered samples as function of (a) holding time at different sintering temperatures and (b) weight percentage of Ti_3SiC_2 .

Fig. 11 AFM images of the Vickers indentation marks under a charge of 5 N for the bulk material obtained after sintering at (a, b) 1300 °C for 10 min and (c, d) 1400 °C for 20 min.

Fig. 12 True stress vs. true strain curves obtained from compression tests of the Ti_3SiC_2 samples sintered under 60 MPa for 20 min at 1300, 1350, and 1400 °C.

process and the fracture surface of the shear-fractured sample were examined. Figure 13 represents the FEG-SEM micro-graphs of fractured surfaces of the bulk samples sintered for 20 min at 1300 °C (Fig. 13(a)), 1350 °C (Fig. 13(b)), and 1400 °C (Fig. 13(c)). As can be observed in Figs. 13(a)–13(c), 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 the transgranular grain fracture. The presence of these two fracture modes confirms the existence of phases with different hardness. Figure 13(d) shows in detail the fractured surface of the sample sintered for 20 min at 1400 °C confirming the layered structure of Ti_3SiC_2 .

The nano-indentation measures enable us to determine both the Berkovich hardness (H) and the Young's modulus (E) of the sintered alloys using curves: load–penetration, hardness–penetration, and penetration–Young's modulus (Fig. 14).

The load–penetration curves show that, applying the same load of about 740 mN, a maximum depth of 1650 nm was obtained for the alloy sintered at 1400 °C for 20 min (Fig. 14(a)). This can be explained by the fact that this material is the most ductile because of its high mass content of Ti_3SiC_2 (~75%).

We notice that the Berkovich hardness, whatever the temperature is, decreases with the increase of the depth. This is, in fact, related to the effect of the material surface. Indeed, the material surface hardens quickly when it undergoes quenching at the end of the SPS

Fig. 13 FEG-SEM micrographs of the fracture surface of the bulk material obtained after sintering for 20 min at (a) 1300, (b) 1350, and (c) 1400 °C. (d) is a detail of (c) confirming the layered structure of Ti_3SiC_2 .

Fig. 14 Variation of (a) load, (b) Berkovich hardness, and (c) Young's modulus as a function of the displacement into surface for samples sintered at different temperatures for 20 min.

cycle. However, the material volume cools more slowly, which makes it less hard than the surface (Fig. 14(b)). It is interesting to note that the Berkovich hardness decreases as the sintering temperature increases. Thus, as an example, for a depth of 1300 nm, when the temperature increases from 1300 to 1400 °C, we note that the Berkovich hardness decreases from 8.72 ± 0.51 to 6.94 ± 0.72 GPa.

From Fig. 14(c), it can be seen that the Young's modulus values vary between 330 ± 20 and 342 ± 14 GPa.

The values of the Berkovich hardness and the Young's modulus found are clearly higher than those

of the pure ternary carbide Ti_3SiC_2 . According to the literature, the pure ternary carbide Ti_3SiC_2 has a Berkovich hardness value of between 5 and 7.3 GPa [36] and a Young's modulus of about 325 GPa [3].

This marked improvement in the Berkovich hardness and Young's modulus is clearly linked to the presence of hard secondary phases such as TiC and SiC .

4 Conclusions

The reactive spark plasma sintering technique was

used for simultaneous synthesis and densification of Ti_3SiC_2 samples from starting powders of 3Ti/2SiC at a relatively low sintering temperature range of 1350–1400 °C, which is much lower than that necessary when using conventional methods.

However, it was found that in all the elaborated samples, Ti_3SiC_2 always coexists with other secondary phases such as SiC and TiSi_2 . Ti_5Si_3 and TiC were intermediate phases in the Ti_3SiC_2 formation process from Ti/SiC. It has been demonstrated that the temperature and the sintering time induce significant effects for promoting Ti_3SiC_2 formation. At 1400 °C for a holding time of 20 min, Ti_3SiC_2 with 75 wt% purity was obtained and the corresponding bulk material had a relative density close to 99.9%. The mechanical properties of the corresponding sample are improved by the presence of the secondary phases. Indeed, its Young's modulus, Vickers hardness, and compressive yield strength were: 330 GPa, 5 GPa, and 1037 MPa, respectively.

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