

Ti₃SiC₂/TiC composites prepared by PDS

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Synthesis of composite materials with improved mechanical properties is considered. Pulse discharge sintering (PDS) technique was utilized for consolidation and synthesis of double phase Ti₃SiC₂/TiC composites from the initial powders TiH₂/SiC/TiC. Scanning electron microscopy with energy-dispersive spectrometry (SEM with EDS) and X-ray diffractometry (XRD) were exploited for the analysis of the microstructure and composition of the sintered specimens. Mechanical tests showed high bending and compression strength and low Vickers hardness of Ti₃SiC₂-rich specimens. The reasons of this behaviour are in the features of the textured microstructure of Ti₃SiC₂ phase.

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1. Introduction

Considerable efforts devoted to the study of metal ceramic Ti₃SiC₂ are in many respects due to the high mechanical characteristics which allow using this material for fabrication of strong, damage tolerant and wear resistant products. Usually when fabricating bulk Ti₃SiC₂ much attention is paid to its purity because the second phase as a rule deteriorates some of the attractive properties of this material such as oxidation [1], chemical resistance, thermal and electrical conductivity [2], etc. Moreover, additional hard phases like TiC or Ti₅Si₃ worsen processing samples made of Ti₃SiC₂ [3]. Unavoidable complication of the synthesis to increase purity of specimens leads to the high cost of production. In our study we tried to overcome this problem by means of production Ti₃SiC₂-based composite with the structure which enabled its relatively low hardness. One of the opportunities to decrease production costs is a proper choice of initial powders. Basically five sets of powders are known to use for the synthesis Ti₃SiC₂ by PDS (Pulse Discharge Sintering) [4]. Most of them utilize Ti as one of the components. In our work we changed TiH₂ for Ti because of significantly lower cost of the former. Since TiH₂ was known both as a catalyst and as a porous making material we assumed that the synthesis could bring about formation of the structure with quite divergent phase content. Before the synthesis of the bulk samples we preliminary considered several powder reactions in a vacuum furnace. After XRD study of the treated powders we chose the initial mixture which yielded the highest percentage of Ti₃SiC₂ and then slightly varying its composition prepared set of the mixtures for the PDS synthesis.

Although the stoichiometric ratio of elements in the starting powders to yield Ti₃SiC₂ should be 3Ti/Si/2C in practice it is not the case. According to [4, 5] the initial mixture Ti/Si/1.5TiC and temperature of the synthesis between 1200 and 1300°C are the optimal starting powders and temperature range, respectively, for obtaining Ti₃SiC₂ of the highest purity in a powder as well as in a bulk state. It should be noted that the other sets of the powders also produced more than 90% of Ti₃SiC₂ at PDS [4]. Starting from these data we prepared following mixtures: (1) 2TiH₂/2Si/3TiC, (2) 3TiH₂/Si/2C, (3) 3TiH₂/SiC/C, (4) 2TiH₂/SiC/0.5TiC.

2. Experimental

The powders were mixed with a mechanical pestle in the mortar with propanol for 3 h. The average particle size after milling and purity of the powders were 1 μm and 99.9% for TiC, 1 μm and 99% for SiC, 5 μm and 99.9% for Si, 5 μm and 99% for C, 5 μm and 97.9% for TiH₂. The mixtures were put in the alumina crucible and treated in the vacuum furnace for 2 h at temperature from 1200 to 1500°C. Pressure during the thermal treatment was below 10⁻² Pa. Before sintering the mixtures were compacted into the graphite molds of 30 and 50 mm diameter. Sintering was performed under pressure 50 MPa and temperature 1300°C after heating with rate about 50°C per minute without preliminary annealing to remove hydrogen. X-ray diffractometry (XRD) with CuKα radiation (30 kV, 40 mA) and scanning electron microscopy with energy-dispersive spectrometry (SEM with EDS) were used for characterization of the sintered materials and calculation of

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their phase content. Vickers hardness was measured under a load of 98 N. Flexural and compression strengths on the specimens with size $35 \times 2 \times 2$ mm and $6 \times 3 \times 3$ mm, respectively, were determined. Measurements of density were performed by Archimedes method. All the tests were conducted at room temperature.

3. Results and discussion

XRD profiles shown in Fig. 1 a, b, c demonstrate low amount of the Ti_3SiC_2 phase in the mixtures after treatment.

Moreover, as opposed to the same reaction based on utilization of Ti as one of the components in the mixture [6] the present reaction of the powders (1) yields TiC and Ti_5Si_3 only. One more feature is a relatively higher content of Ti_3SiC_2 after processing the $4TiH_2/2SiC/TiC$ starting powders (Fig. 1d). These results showed that the mechanism of the reactions after substitution of TiH_2 for Ti changed. In some publications [7, 8] the authors emphasized that additional amount of silicon favoured the synthesis of Ti_3SiC_2 due to high diffusivity of Si atoms. In another publication it was stated that the synthesis of Ti_3SiC_2 from powders (1) occurred in liquid Ti-Si phase [9]. In both cases necessary condition for the synthesis of Ti_3SiC_2 was existence of liquid Si at temperature of the reaction. In our case contrary to Ti, TiH_2 as a catalyst accelerated the reaction between the components in mixtures (1), (2) and (3). As a result during heating all silicon and carbon reacted with TiH_2 to form Ti_5Si_3 and TiC at temperatures lower than the reaction temperature, and, practically, no liquid Si ex-

isted at the targeted temperature. It caused low yield of Ti_3SiC_2 eventually. Since at heating the carbides are not so reactive as the elemental powders final powder after processing the initial mixture (4) incorporated more Ti_3SiC_2 than after processing the mixture (3) [10].

Taking into account abovementioned results we prepared several mixtures of TiH_2 , SiC, TiC powders with a different molar ratio of the constituents. These compositions were mainly chosen to satisfy the molar ratio $2TiH_2/SiC/0.5TiC$.

Fabrication of the specimen through reaction of the powders of $TiH_2/SiC/TiC$ is scarcely mentioned in the literature [11]. The layered structure which is observed in Ti_3SiC_2 represents two octahedral Ti_6C cell separated from the neighbouring ones by Si layer. Linking them was proposed as one of the model of the crystal growth in Ti_3SiC_2 [12]. It can be achieved owing to the reaction $SiC + Ti \rightarrow Si + TiC$. Because of Si evaporation it is necessary to add some excess of SiC to have the molar ratio SiC/TiC greater than adopted in the stoichiometric mixture $2TiH_2/SiC/TiC$.

In most of the compositions presented in Table I there is a double amount of started TiH_2 powder as compared to SiC one. This proportion at various TiC content could make clear the role of TiC in the synthesis process. Three specimens TH6, TH7, TH8 were synthesized to find out the effect of TiH_2/SiC ratio on the composition and the material properties of the sintered specimens.

In Fig. 2 XRD pictures of TH1, TH2, TH4 and TH7 are shown. All XRD profiles demonstrate availability of two phases only: TiC and Ti_3SiC_2 . Intensity ratio of Ti_3SiC_2 and TiC peaks as well as relative intensities of

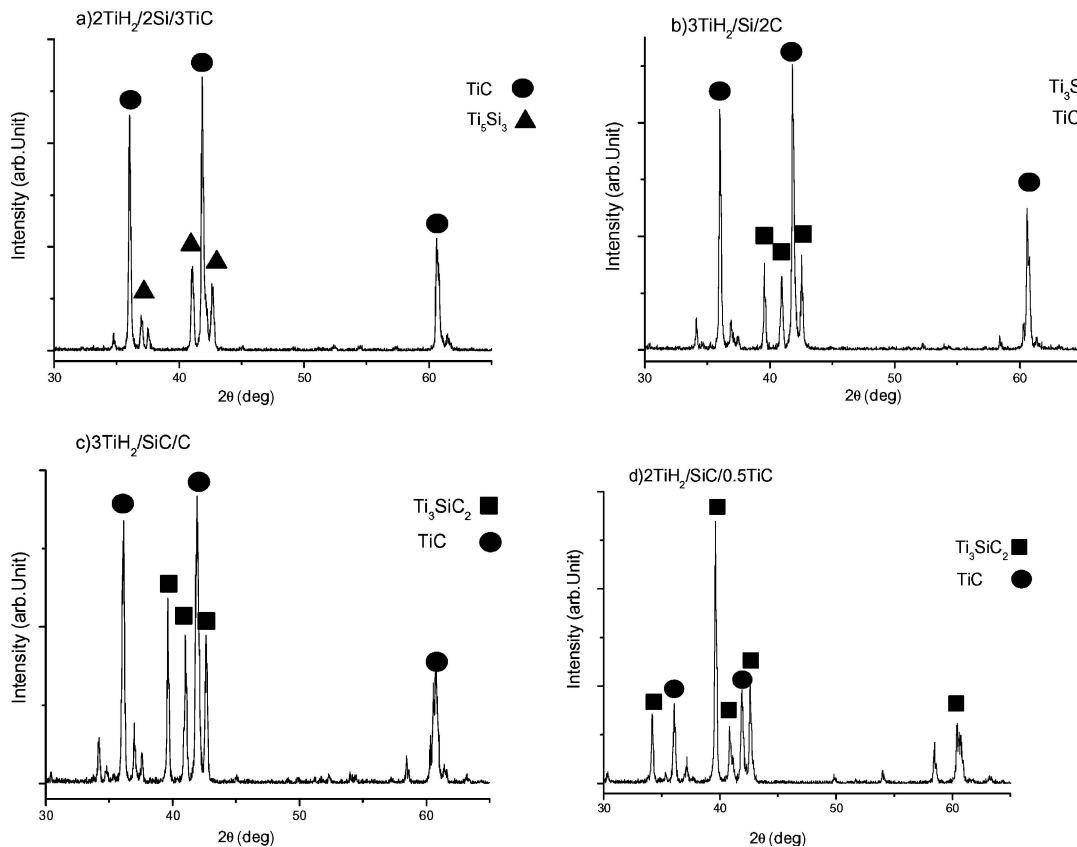


Figure 1 X-ray diffraction patterns of the powders after thermal processing.

TABLE I Compositions of the initial mixtures

Specimen	Molar ratio of the initial powders		
	TiH ₂	SiC	TiC
TH 1	2	1	1
TH 2	2	1	0.75
TH 3	2	1	0.7
TH 4	2	1	0.65
TH 5	2	1.15	0.65
TH 6	2	0.9	0.6
TH 7	2	1	0.6
TH 8	2	1.15	0.6
TH 9	2	1	0.5

Ti₃SiC₂ peaks vary according to the initial composition. XRD pattern of the specimen TH1 sintered from the powders in stoichiometric ratio (Fig. 2a) displays that (104) is the highest intensity peak among the other Ti₃SiC₂ peaks and is several times as high as the next one (008) whereas in the other compounds (Fig. 2b–d) (008) is commensurable with (104).

High intensity of (008) peak in the diffraction patterns of TH2, TH4 and TH7 reveals existence of (001) texture in the Ti₃SiC₂ phase of these specimens as a result of preferential grain growth along (001) plane. As discussed in [13, 14] pressure during synthesis rotates basal (001) plane of grain into perpendicular to load direction strengthening (008) diffraction peak. It is worth noting that on XRD patterns of the specimens sintered by PDS technique with different reaction paths [15] including that of specimen synthesized from the initial 4Ti/2SiC/TiC mixture (104) peak is clearly dom-

inant over the other Ti₃SiC₂ ones. By this means the substitution of TiH₂ for Ti in the reaction of the powders Ti/SiC/TiC favours growth of the oriented crystals in specimens sintered from TiC depleted starting mixtures.

The micrographs displayed in Fig. 3 represent the typical Ti₃SiC₂-rich (a), and TiC-rich (b) microstructures. TiC and Ti₃SiC₂ grains have dark grey and bright grey colors, respectively, and different size in the Ti₃SiC₂-rich specimens. Their Ti₃SiC₂ grains range from 5 to 40 μm in length and from 3 to 20 μm in width. TiC grains are smaller, less than 5 μm. They are mainly placed near borders of Ti₃SiC₂ grains as it can be seen from Fig. 3a. Because of appearance of a big amount of the TiC phase in the specimen TH1 Ti₃SiC₂ grain growth was suppressed, and as a result their size in this specimen does not exceed 10 μm.

The phase content of the specimens was calculated from the ratio of areas occupied by each phase (Table II). In the specimens synthesized from the powders with 2TiH₂/SiC molar ratio except TH1 volume fractions of Ti₃SiC₂ are mainly between 65 and 80%. It can be concluded from these results that TiH₂/SiC ratio predominantly determines composition of the fabricated specimens. It is especially clear by comparison of the specimens TH2 and TH9: although TiC content in the initial mixture of the specimen TH2 is half much again that of the TH9, after sintering both specimens possess near the same phase content. High sensitivity of the phase content to the molar ratio TiH₂/SiC is obvious from comparison of the TiC volume fractions of the TH7 and the TH8 specimens as well as the TH4 and the TH5. They were synthesized from the powders with

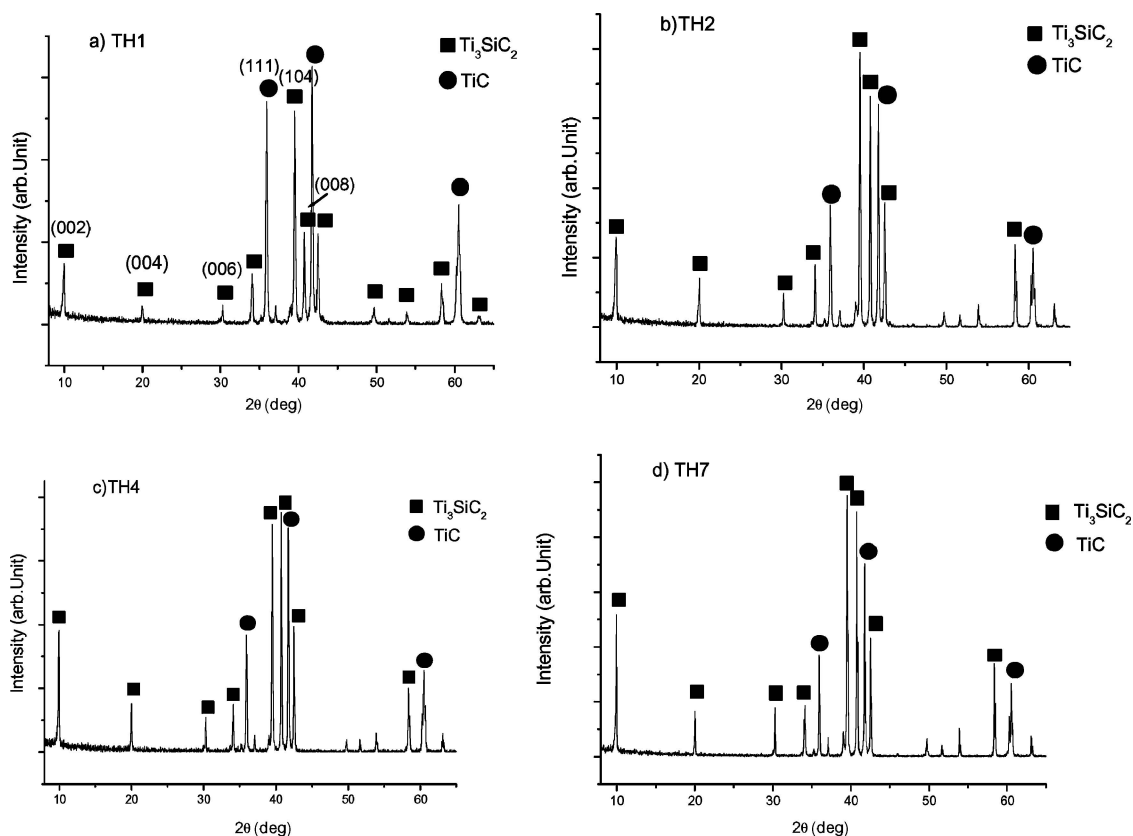


Figure 2 X-ray diffraction patterns of the sintered specimens.

TABLE II Material properties of the studied composites

Specimens	Phase content (Vol.%)			Measured density g/cm ³	Theoretical density g/cm ³	Vickers hardness (GPa)	Bending strength (MPa)	Compression strength (MPa)
	Ti ₃ SiC ₂	TiC	SiC					
TH 1	34	65	<1	4,63	4,78	9,77		
TH 2	80	20		4,6	4,61	5,13		
TH 3	67	33		4,61	4,65	4,77	553	1540
TH 4	64	36		4,61	4,66	4,15		
TH 5	45	54	1	4,61	4,73	9,07		
TH 6	65	35		4,57	4,66	5,92		
TH 7	77	23		4,57	4,61	4,05	417	
TH 8	42	58		4,72	4,75	6,2		
TH 9	63	37		4,59	4,67	5,85	440	1500

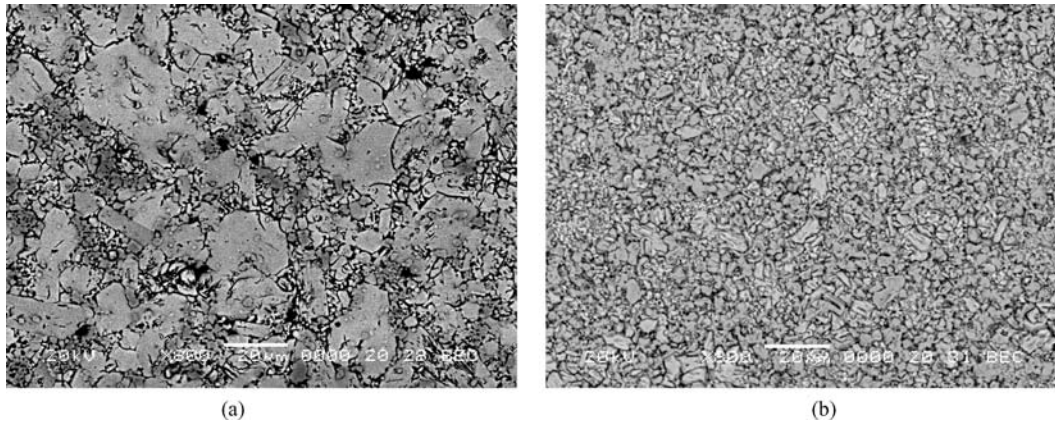


Figure 3 SEM (backscattered electron mode) images of the specimens (a) TH2 and (b) TH1.

the same TiH₂/TiC ratio but different TiH₂/SiC one. The moderate deviation from 2TiH₂/SiC ratio causes an increase in the TiC fraction of 35 and 20 vol.%, respectively. It should be noted that abovementioned relationship between the mixture composition and the phase content of the specimens after PDS synthesis is not true for the TH1, probably, because of lack of SiC as compared to TiC in the mixture.

Mechanical properties of the specimens summarized in Table II demonstrate ability of the materials to adopt significant deformation without failure. Bending strength of these composites exceeds that of Ti₃SiC₂ except fine grained one [16–19] because of strengthening by the TiC phase. Compression strength of them is the highest one among the others reported before [19–21] whereas Vickers hardness mostly lies in the range 4–6 GPa. In some of the samples studied significant amount (more than 40 vol.%) of TiC seriously deteriorates machinability (Fig. 4) but in the whole their machinabilities are the best among the specimens having near the same or even higher content of Ti₃SiC₂ [3, 16, 20].

Moreover, as it is pointed out in [22] Vickers hardness 4–6 GPa are intrinsic to almost pure Ti₃SiC₂. Fig. 4 represents hardness of the specimens as a function of ratio TiH₂/TiC in initial powders. It is apparent that hardness changes with the phase content of the specimens which in its turn correlates with starting powder ratio that was mentioned earlier.

In the literature there were some scientific reports [14, 23] concerned with mechanism providing high

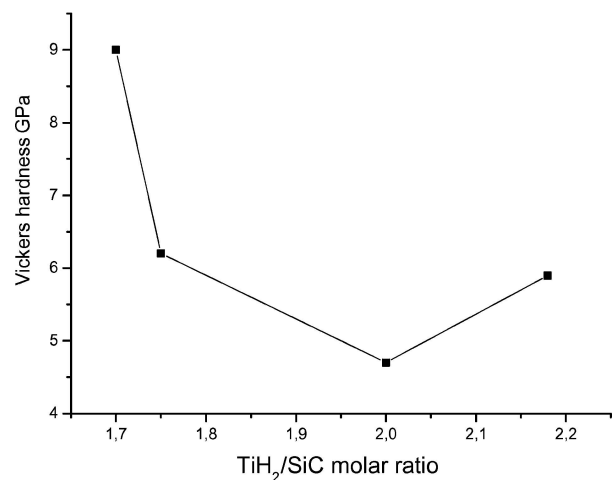


Figure 4 Correlation between molar ratio TiH₂/SiC in initial mixtures and Vickers hardness of the specimens sintered from these mixtures.

mechanical strength of Ti₃SiC₂ and its relatively low hardness. These mechanisms are reported to be based on laminated structure of Ti₃SiC₂ and its ability to form kink band and delamination as a response to stress. Taking into account that the microstructure of the specimens studied in this paper and having low hardness from the most part consists of Ti₃SiC₂ grains we can assume these mechanisms to be responsible for high machinability. This feature can be attributed to the textured microstructure of the Ti₃SiC₂ phase in the studied Ti₃SiC₂-rich specimens which favours kink band development because in this case

Ti₃SiC₂ basal planes (001) are parallel to surface of specimens.

In previous publications [16, 24] TiH₂ was utilized as one of the starting powders for the synthesis of Ti₃SiC₂ by hot pressing only after long time (~6 h) preliminary annealing to remove hydrogen. The main obstacle for direct using of this hydride was its high ability to make pores during decomposition above 750°C. Although micrographs (Fig. 3) did not show porous structure of the composites, additional Archimedes test was conducted to ensure to it. Results confirmed that specimens possessed compact structure and as is seen from Table II their densities are close to the theoretical ones exceeding 97% of them for the present phase contents. The absence of voids probably arose from lack of sealing during the synthesis so that released hydrogen penetrated through graphite mold at increase of temperature. Similarly, it is almost impossible during HIP synthesis. In this case hydrogen can not release from capsule where reaction occurs and resultant material acquires porous structure.

4. Conclusions

In summary, the samples synthesized by PDS method from TiH₂/SiC/TiC powders demonstrate good performance exhibiting high bending strength of 400–600 MPa as well as high compression strength of 1500 MPa. These excellent mechanical characteristics are provided by high content of TiC phase. Nevertheless, even at 20–35% of TiC specimens exhibit low Vickers hardness (4–6 GPa). The low hardness is accomplished by the textured microstructure with (001) texture and providing that initial mixtures have 2TiH₂/SiC ratio and low content of TiC powder. The unusual combination of high mechanical strength and low hardness, low cost of source materials and relatively short time of sintering reveals this route as feasible one for fabricating composites with high performance.

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