Solid–liquid reaction synthesis and thermal stability of Ti$_2$SnC powders

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A novel method based on the solid–liquid reaction in the Ti–Sn–C system was developed for the synthesis of Ti$_2$SnC powders. In this process, Ti–Sn intermetallic compounds were formed in liquid Sn, then they further reacted with graphite powders to form Ti$_2$SnC. The advantages of this solid–liquid reaction based method include low synthesis temperature, short reaction time and less impurity in the as-prepared powders. Investigations on the stability of Ti$_2$SnC powders demonstrated that Ti$_2$SnC was stable in Ar up to at least 1200 °C. In air, however, a complex oxidation–decomposition–oxidation process was observed.

1 Introduction

Recently a new family of layered ternary carbides referred to as '211' or 'H-phase' compounds attracted the attention of material scientists as well as physicists and chemists. The preliminary work demonstrated[1,2] that H-phase materials exhibit a number of properties including high strength and modulus, damage tolerance at room temperature, high thermal and electrical conductivity, being readily machinable by high speed steel tools. The unique combination of these properties makes H-phase materials promising candidates in diverse applications. Ti$_2$SnC is one of the layered ternary carbides from this family. Ti$_2$SnC was first identified by Jeitschko *et al.* in 1963.[3] They proposed a crystal structure isotopic with Cr$_2$AlC and a hexagonal symmetry with a space group of *P*6$_3$/*mmc* and lattice parameters of *a* = 0.3186 nm and *c* = 1.363 nm. Fig. 1 shows the crystal structure of Ti$_2$SnC. The structure consists of alternating layers of Ti$_6$C octahedra and two-dimensional

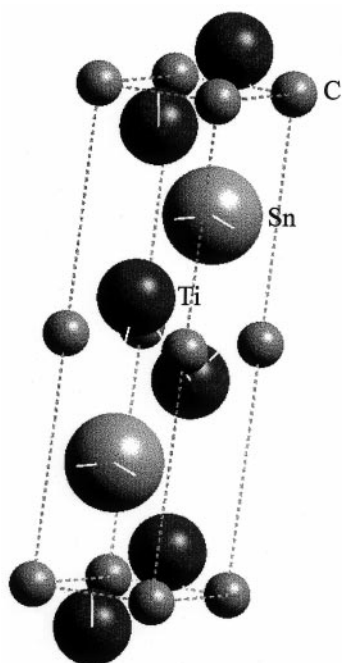**Fig. 1** Crystal structure of Ti$_2$SnC.

closed-packed layers of Sn. There have been only a few other papers published on Ti$_2$SnC.[2,4] Vincent *et al.*[4] examined the lattice parameters of Ti$_2$SnC using the Rietveld technique and obtained lattice parameters of *a* = 0.3162 nm and *c* = 1.36789 nm, which are slightly different from those given by Jeitschko *et al.*[3] Vincent *et al.*[4] also established the isothermal section of the Ti–Sn–C phase diagram at 1200 °C.

Recent interest in Ti$_2$SnC was stimulated by the disclosure of the unusual properties in layered ternary compounds like Ti$_3$SiC$_2$, Ti$_3$GeC$_2$ and Ti$_2$AlC.[5–8] Barsoum *et al.*[2] prepared polycrystalline Ti$_2$SnC using hot isostatic pressing (HIP) of Ti, Sn, and C elemental powders. The material was reported to exhibit a Vickers hardness of 3.5 GPa and electrical conductivity of 14 × 10^6 Ω^{-1} m^{-1}. The electrical conductivity of Ti$_2$SnC was much higher than those of other layered ternaries like Ti$_3$SiC$_2$, Ti$_2$AlC, Zr$_2$SnC and Hf$_2$SnC.[1,2,5] The high electrical conductivity combined with the high modulus makes Ti$_2$SnC a useful reinforcement for metals and polymers. Incorporation of such a kind of carbide into the metal matrix will enhance the strength and modulus of the metal[9] without loss of conductivity. Methods for the preparation of Ti$_2$SnC powders, however, have not been well established. One of the problems in the fabrication of the layered ternary carbides like Ti$_2$SnC is that at low temperatures (*e.g.* 1000 °C) the reaction kinetics for the formation of the ternaries are slow, while at higher temperatures (1350 °C) they tend to dissociate. Thus new methods for preparing Ti$_2$SnC powders need to be developed. In this paper, we describe in detail a novel method based on the solid–liquid reaction in the Ti–Sn–C system for the synthesis of Ti$_2$SnC powders. The term solid–liquid reaction was used here to differ it from solid state reaction, wherein no liquid phase formed during the reaction. Our previous work[10] demonstrated that by the addition of the easy liquid forming phase NaF to the Ti–Si–C system, it was favorable for the synthesis of Ti$_3$SiC$_2$ powders. Based on this fact, the solid–liquid reaction synthesis method was developed and used for preparing Ti$_3$SiC$_2$,[11,12] providing the advantages of low synthesis temperature, short reaction time and fewer impurities. In the Ti–Sn–C system, because of the low melting point of Sn, the reaction for the formation of Ti$_2$SnC is a solid–liquid process. In the following sections, the reaction path and advantages of the solid–liquid synthesis of Ti$_2$SnC are discussed. The thermal stability of the Ti$_2$SnC powders in Ar and air was also investigated.
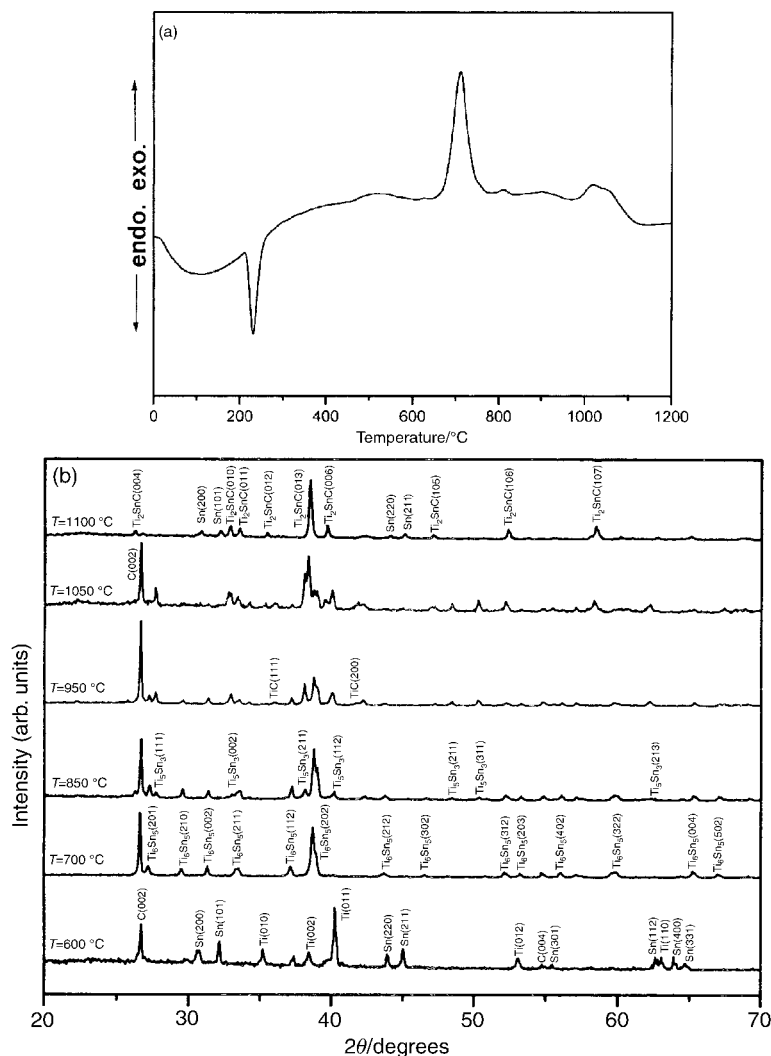
Fig. 2 (a) DTA curve of a stoichiometric mixture of Ti, Sn and C powders. (b) X-Ray diffraction patterns of a stoichiometric mixture of Ti, Sn and graphite powders after heating to different temperatures.

2 Experimental

The starting materials used for the preparation of Ti_2SnC were Ti, Sn and graphite powders. Before synthesizing the Ti_2SnC powders, differential thermal analyses (DTA) were conducted in order to identify the reactions during the heating of Ti–Sn–C powder mixtures. The stoichiometric mixture of Ti, Sn and graphite powders was heated at a rate of $10\,°C\,min^{-1}$ to $1200\,°C$ in Ar atmosphere in a Pyris 7 DTA apparatus (Perkin-Elmer Instruments, USA) and the DTA curve was recorded. In parallel runs, the powder mixtures were heated to the temperature at which an exothermic or endothermic reaction peak appeared in the DTA curve, and held at that temperature for 1 h. After cooling to room temperature, the reaction products were examined by X-ray diffraction (XRD) in order to identify the exact reactions that took place in the heating process.

Ti_2SnC powders were prepared *via* the following procedure. Ti, Sn and graphite powders with near stoichiometric compositions were mixed in a polypropylene jar for 10 hours, pressed into a pellet and then were placed in an Al_2O_3 crucible. The reaction synthesis of Ti_2SnC powders was performed in a SiC tube furnace by heating the powder mixture to $1150\,°C$ at a rate of $10\,°C\,min^{-1}$ in Ar atmosphere and held at this temperature for 2 hours. The as-prepared powders were purified and were analyzed by XRD. Pure Ti_2SnC powders were obtained by immersing the as-prepared powders in hot HCl solution and washing with distilled water. X-Ray

diffraction data were collected by a step-scanning diffractometer (Rigaku D/max-A, Japan) using Cu Kα radiation. To carry out a refinement of the lattice constants, the corrected positions with accuracy better than $0.02°$ were used. The refinement of the lattice parameters was done using the Rietveld method[13] and the DBWS code[14] from the Cerius^2 computer program for material research (Molecular Simulations Inc., USA).

The thermal stability of Ti_2SnC in both Ar and air was investigated. In order to characterize the thermal stability of Ti_2SnC, techniques such as DTA, TGA and XRD were used. DTA curves were recorded by heating the pure Ti_2SnC powders at $10\,°C\,min^{-1}$ in either Ar or air atmosphere to $1200\,°C$. Mass changes as a function of time at different temperatures ($300–650\,°C$) in air were measured. The phase composition of the powders after oxidation in air was examined by XRD.

3 Results and discussion

3.1 Synthesis of Ti_2SnC powders

The DTA curve of a stoichiometric mixture of Ti, Sn and C powders is shown in Fig. 2(a). The endothermic peak at $230\,°C$ is associated with the melting of Sn. Because of the melting of Sn, further reactions in the Ti–Sn–C system were in the melt of Sn. At $700\,°C$, an exothermic peak was observed, which was associated with the formation of Ti_6Sn_5. To confirm our
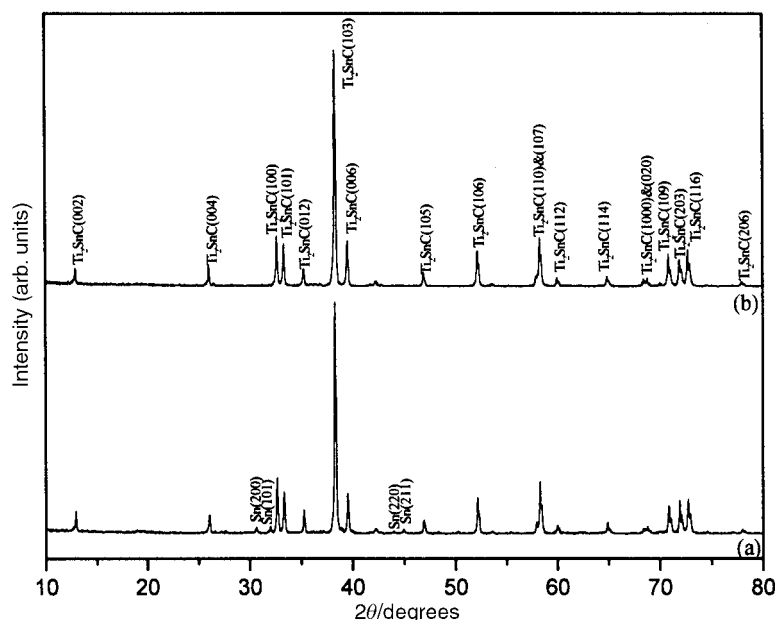
Fig. 3 X-Ray diffraction patterns of the as-prepared (a) and purified (b) Ti$_2$SnC powders.

assumption, Ti, Sn and graphite powders were heated to 700 °C and held at that temperature for one hour. X-Ray diffraction analysis revealed that the main phases in the powders treated at 700 °C were Ti$_6$Sn$_5$ and graphite (Fig. 2(b)). Thus the exothermic peak at 700 °C was attributed to the formation of Ti$_6$Sn$_5$. At 850 °C both Ti$_6$Sn$_5$ and Ti$_5$Sn$_3$ were identified. The exothermic peak at about 950 °C in Fig. 2(a) was related to the formation of TiC. The small exothermic peak at 1050 °C corresponded to the formation of Ti$_2$SnC. From the above analysis the reaction path for the formation of Ti$_2$SnC was suggested to be: Ti + Sn + C/Ti$_6$Sn$_5$ + C/Ti$_6$Sn$_5$ + Ti$_5$Sn$_3$ + C/Ti$_6$Sn$_5$ + Ti$_5$Sn$_3$ + TiC + C/Ti$_2$SnC + Sn.

The above results demonstrated that Ti$_2$SnC could be prepared at above 1100 °C using the solid–liquid reaction in the Ti–Sn–C system. Based on the results of DTA and XRD analysis, Ti$_2$SnC powders were synthesized using a near-stoichiometric mixture of Ti, Sn and graphite powders. The powder mixture was heated at 10 °C min^{-1} to 1150 °C in flowing Ar atmosphere and held at this temperature for two hours. After cooling to room temperature, the powders were ground in an agate mortar and pestle and examined by XRD. Fig. 3 shows X-ray diffraction patterns of the as-prepared (a) and purified Ti$_2$SnC powders (b). It is seen from the figure that no impurities such as TiC and Ti$_6$Sn$_5$ were identified. The only impurity was a very small amount of Sn, which could be removed by immersion of the as-prepared powders in hot HCl solution. TiC or Ti$_6$Sn$_5$ impurities were observed to co-exist with Ti$_2$SnC in previous works.[2,4] Although Ti$_6$Sn$_5$ is removable by washing the powders with hot HCl solution, TiC is really difficult to remove. Therefore, avoiding the formation of TiC is important. Since TiC is unstable in liquid metametals[15] and transformed into layered ternary carbides, in the solid–liquid reaction synthesis method formation of TiC can be avoided by adding surplus Sn.

To confirm the phase synthesized through the solid–liquid reaction was Ti$_2$SnC, Rietveld analysis[13,14] of the purified

powders was conducted. Ti$_2$SnC crystallizes in a hexagonal structure. The space group is $P6_3/mmc$ with Ti at (4f), Sn at (2d) and C at (2a) Wyckoff positions. Lattice parameters of $a = 3.1625$ Å and $c = 13.678$ Å were calculated from the refinement. The final reliability factors from the Rietveld refinement are $R_P = 8.6\%$ and $R_{WP} = 12.4\%$. The lattice constants calculated in the present work agree well with those of Barsoum *et al.*[2] and Vincent *et al.*[4] Table 1 lists the lattice parameters of Ti$_2$SnC obtained by different authors. Table 2 lists the reflections, d-spacings and intensities for the experimental and calculated X-ray diffraction patterns from Rietveld analysis. For comparison, the data from the relevant JCPDS card[16] are also given in Table 2. The results clearly show that the powders synthesized by the solid–liquid reaction in the Ti–Sn–C system are Ti$_2$SnC. Fig. 4 shows a SEM micrograph of the Ti$_2$SnC powders after treatment in hot HCl solution. The figure demonstrates that the crystallite size of Ti$_2$SnC powders prepared by the solid–liquid reaction synthesis method was less than 1 μm. Similar to our previous work[11,12] in preparing Ti$_3$SiC$_2$, the present work demonstrates that solid–liquid reaction synthesis is a novel method for the synthesis of Ti$_2$SnC powders. The synthesis temperature is 50–200 °C lower than that used in the early works[2,4] and the level of impurity is lower.

3.2 Thermal stability of Ti$_2$SnC

Understanding the thermal stability is of vital importance in the application of Ti$_2$SnC. In this work, we investigated the high temperature stability of Ti$_2$SnC in both Ar and air. Fig. 5 shows the DTA curves of Ti$_2$SnC during heating in both Ar and air, respectively. It is seen that the DTA curve of Ti$_2$SnC in Ar is quite flat with no peaks up to 1200 °C; the TGA curve shows no apparent weight loss during the heating process. Analyzing the phase composition of Ti$_2$SnC powders after heating to 1200 °C, we find no phases other than Ti$_2$SnC, indicating that no decomposition occurred during the heating of Ti$_2$SnC powders in Ar. Thus Ti$_2$SnC is believed to be stable in Ar atmosphere up to at least 1200 °C.

The DTA curve of Ti$_2$SnC in air, however, shows an exothermic peak beginning at about 300 °C, which is attributed to the oxidation of Ti$_2$SnC. The exothermic peaks extended to a wide temperature range indicating that the oxidation of Ti$_2$SnC is a complex process. To understand the oxidation process, isothermal oxidation of Ti$_2$SnC powders from 300 to 650 °C

Table 1 Lattice parameters of Ti$_2$SnC obtained by different authors

Lattice parameters/Å	References
$a = 3.186$, $c = 13.63$	Jeitschko *et al.* 1963[3]
$a = 3.1635$, $c = 13.675$	Barsoum *et al.* 1997[2]
$a = 3.1626$, $c = 13.679$	Vincent *et al.* 1998[4]
$a = 3.1625$, $c = 13.678$	This work

Table 2 Experimental and calculated reflections, 2θ positions and intensities of Ti_2SnC

Reflection (hkl)	$2\theta_{cal.}/°$	$2\theta_{obs.}/°$	$I/I_{0cal.}$ (%)	$I/I_{0obs.}$ (%)	$2\theta_{ref.}/°$	$I/I_{0ref.}$ (%)
004	25.926	25.911	8.66	7.68	26.05	11
010	32.551	32.538	20.65	17.90	32.69	22
011	33.218	33.205	15.91	14.44	33.36	17
012	35.153	35.141	6.7	8.20	35.29	7
013	38.188	38.177	100	100	38.33	100
006	39.387	39.375	16.06	17.60	39.52	19
014	42.125	42.115	1.98	2.97	42.27	2
015	46.787	46.778	4.38	6.05	46.93	6
016	52.044	52.037	17.50	18.08	52.19	15
008	53.444	53.437	0.74	1.45	53.58	1
017	57.811	57.806	6.23	6.11	57.96	4
110	58.178	58.174	28.13	27.33	58.34	19
112	59.872	59.868	3.66	4.61	60.04	3
018	64.044	64.042	0.29	0.74	64.20	1
114	64.792	64.790	7.33	6.37	64.96	4
020	68.327	68.327	3.84	3.84	68.50	2
00 10	68.438	68.436	0.92	0.86	68.58	1
021	68.717	68.717	3.45	3.14	68.89	2
022	69.881	69.882	1.41	1.48	70.06	1
019	70.735	70.735	21.19	19.18	70.89	15
023	71.804	71.805	24.06	22.53	71.98	14
116	72.594	72.595	27.30	24.61	72.77	17
024	74.461	74.463	0.76	1.17	74.64	1
025	77.828	77.832	1.80	1.73	78.01	1
01 10	77.908	77.911	1.83	1.65	78.07	1

cal stands for calculated data, obs for observed experimental data, ref is data from JCPDS card.

was performed. After oxidation the powder samples were characterized by XRD. The results demonstrated that oxidation of Ti_2SnC started at 300 °C and it was totally oxidized at above 650 °C. So, Ti_2SnC exhibited a rather limited oxidation resistance.

Fig. 6 shows the isothermal relative mass variation $\Delta m/m_0$ versus time at different temperatures. It shows that in all runs the mass change versus time curves exhibit two step features. The first step ($t < 10$–30 min) corresponds to very rapid oxidation kinetics, the weight gain varying from 2 to 30% depending on the temperature. The second step is a slow oxidation process. An interesting phenomenon is that in the second step of oxidation, the weight gain of the sample treated at 500 °C is less than that for the sample treated at 450 °C. The reason for this phenomenon is not understood but might be related to the structure change of Ti_2SnC. By analysis of the X-ray diffraction patterns of samples treated at different temperatures, we find that the detected crystalline phases in the oxidized samples are quite different. In the sample oxidized below 500 °C, Ti_2SnC as well as a small amount of SnO_2 were identified (as shown in Fig. 7). In the samples treated at 500 °C

and 550 °C, however, Sn, SnO_2, TiC_x and Ti_2SnC were identified. In samples treated at 600 and 650 °C, the main phases were SnO_2 and TiO_2. We assume that decomposition of Ti_2SnC occurred at about 500 °C, then oxidation of TiC_x and Sn took place. At this point, two questions must be answered. The first is why Sn existed after treating the samples at temperatures above 500 °C in air. The second question is whether the decomposition of Ti_2SnC at temperatures above 500 °C was induced by the oxidation. In other words, whether it is an oxidation–decomposition–oxidation or a decomposition–oxidation process. To make sure that Sn existed in the sample after treatment above 500 °C in air, bulk Ti_2SnC was heated in air to 550 °C for 4 hours. Strong reflections of Sn are seen in the X-ray diffraction pattern of the bulk sample after the treatment, as shown in Fig. 8. Thus the presence of Sn was confirmed. However, the reason why Sn was stable at above 500 °C is still unknown and needs further investigation. The solution to the second question can be found by comparing the phase compositions of Ti_2SnC treated in Ar and air. Since Ti_2SnC was stable in Ar up to at least 1200 °C, the decomposition of Ti_2SnC is assumed to be an oxidation-
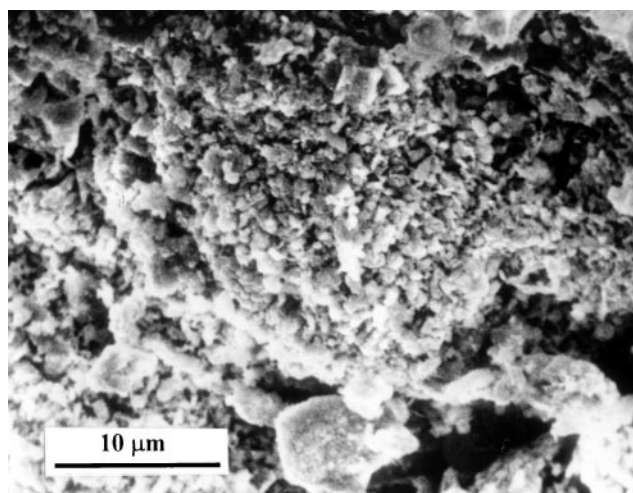

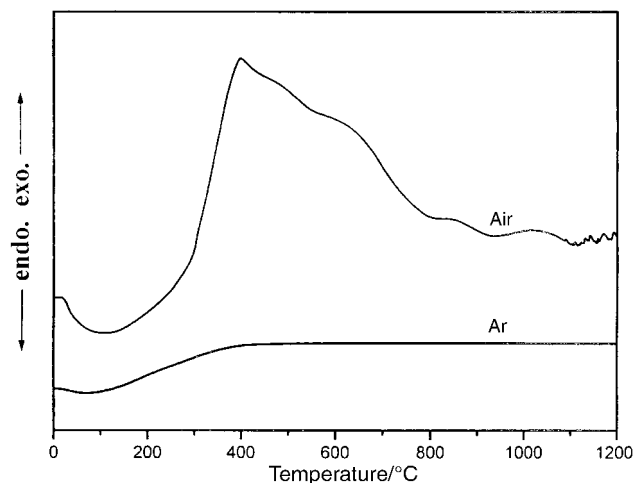**Fig. 4** SEM micrograph of purified Ti_2SnC powders.

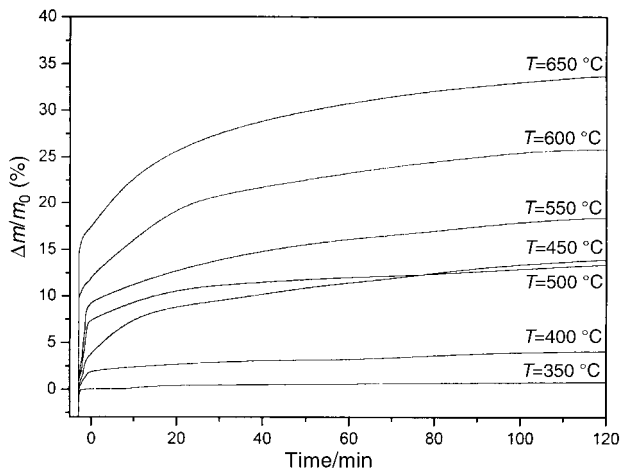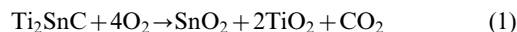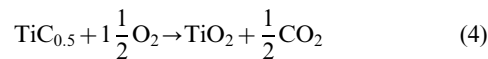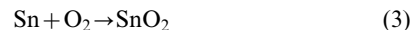**Fig. 5** DTA curves of Ti_2SnC in Ar and air, respectively.

Fig. 6 Relative mass change *versus* time for Ti₂SnC during exposure at different temperatures in air.

induced process. Thus the oxidation of Ti₂SnC was considered as an oxidation–decomposition–oxidation procedure. At temperatures below 500 °C, oxidation of Ti₂SnC dominated; while at temperatures above 500 °C, because of the dissociation of Ti₂SnC, oxidation of TiC$_x$ and Sn dominated. From the above analysis, the complex oxidation process of Ti₂SnC can be described as:

Below 500 °C

$$Ti_2SnC + 4O_2 \rightarrow SnO_2 + 2TiO_2 + CO_2 \tag{1}$$

Above 500 °C

$$Ti_2SnC \rightarrow 2TiC_{0.5} + Sn \tag{2}$$

$$Sn + O_2 \rightarrow SnO_2 \tag{3}$$

$$TiC_{0.5} + 1\frac{1}{2}O_2 \rightarrow TiO_2 + \frac{1}{2}CO_2 \tag{4}$$

where TiC$_{0.5}$ is used instead of TiC$_x$ for simplicity. We must acknowledge that the mechanism for the oxidation of Ti₂SnC is
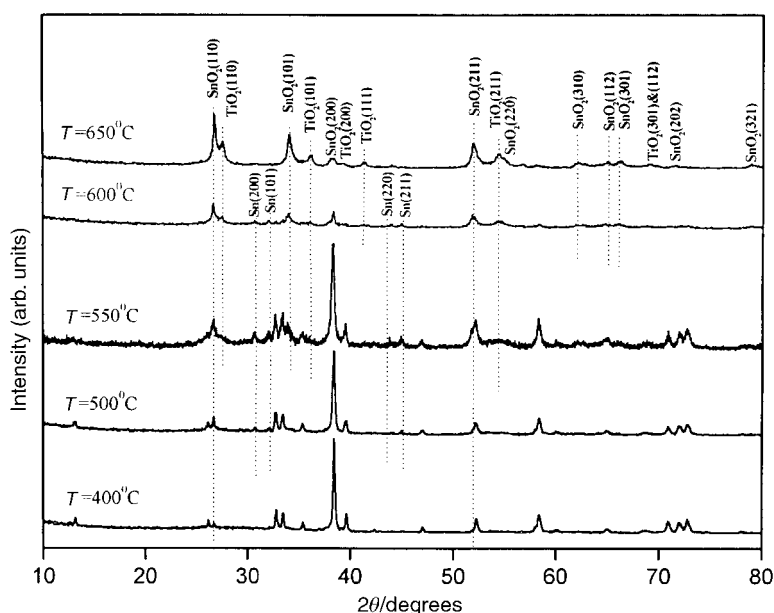

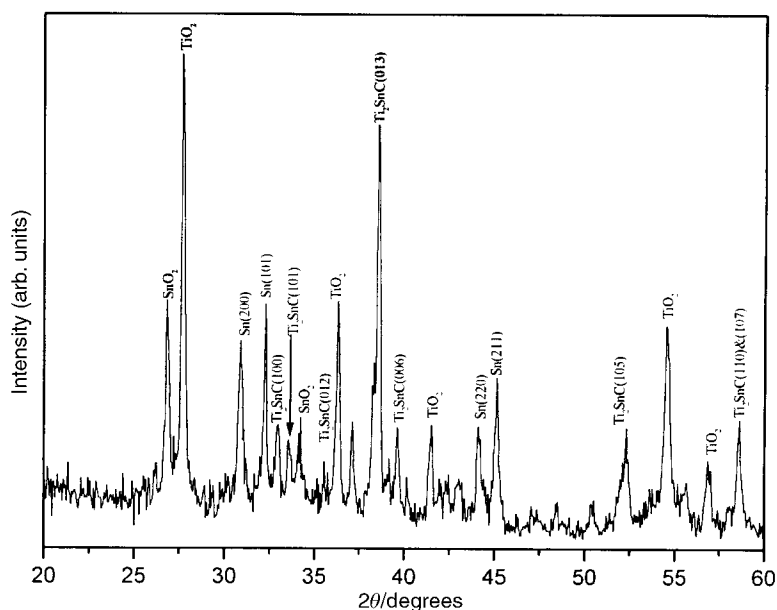**Fig. 7** X-Ray diffraction patterns of Ti₂SnC powders after exposure to air at different temperatures.

Fig. 8 X-Ray diffraction pattern of bulk Ti₂SnC after treatment at 550 °C for 4 hours in air.

not well understood. Work is ongoing in the authors' group to investigate the oxidation mechanism of Ti_2SnC using bulk material. The limited oxidation resistance implies that Ti_2SnC can be used in a protective environment or in an oxygen-rich atmosphere below 500 °C.

4 Conclusion

A novel method based on the solid–liquid reaction in the Ti–Sn–C system has been developed for the synthesis of Ti_2SnC powders. In this process, Sn melts at 230 °C which provides a liquid phase for the heat transfer and reactions in the Ti–Sn–C system. Ti reacts with liquid Sn to form Ti–Sn compounds and then the Ti–Sn compounds react with graphite to form Ti_2SnC. The advantages of this solid–liquid reaction based method include low synthesis temperature, short reaction time and fewer impurities in the as-prepared powders. Investigations into the thermal stability of Ti_2SnC powders demonstrate that Ti_2SnC is stable in Ar up to at least 1200 °C but undergoes a complex oxidation–decomposition–oxidation process in air.

Acknowledgements

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