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Bimodal Microstructure and Reaction Mechanism of Ti_2SnC Synthesized by a High-Temperature Reaction Using Ti/Sn/C and Ti/Sn/TiC Powder Compacts

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High purity of titanium tin carbide (Ti_2SnC) powder was fabricated by pressureless sintering two types of mixtures of Ti/Sn/C and Ti/Sn/TiC powders under different conditions. A bimodal microstructure of Ti_2SnC with plate-like and rod-like forms was first observed, which is determined by the grain growth rate in different planes, the C particle's size, and the growth environment. Based on the microstructure observation, a reaction model was proposed to understand the reaction mechanism for the formation of Ti_2SnC. Further investigation of the thermal stability of Ti_2SnC demonstrates that Ti_2SnC decomposes to TiC and Sn in vacuum atmosphere at 1250°C.

I. Introduction

Titanium tin carbide (Ti_2SnC) is one of the most interesting materials in the family of the layered ternary compounds $M_{n+1}AX_n$ ($n = 1, 2, 3$), where M is a transition metal, A is a group IIIA or IVA element, and X is C or N.[1]

Ti_2SnC has been proved to exhibit a number of excellent properties.[1–5] It has low hardness ($\sim$3.5 GPa), high electrical conductivity ($\sim 14 \times 10^6$ $(\Omega \cdot m)^{-1}$), self-lubricity, machinability, etc. In addition, it is damage tolerant at room temperature, resistant to corrosion, and stable up to at least 1200°C. The combination of these properties makes this material a promising candidate in diverse applications in reinforcements for electrical composites, rotating electrical contacts, bearings, and other components for the chemical and petrochemical industries. Hence, it has attracted much worldwide attention.

Up to now, only hot isostatic pressing (HIP),[3,4] hot pressing (HP),[3] and pressureless sintering techniques[6,7] have been adopted to fabricate Ti_2SnC powders from a stoichiometric mixture of Ti/Sn/C powders. However, high purity of the Ti_2SnC powder is difficult to obtain by adopting the above-mentioned methods and the mixture, because impurities such as TiC, Ti–Sn compounds, or Sn always accompany Ti_2SnC. The disadvantages of the existing impurities, especially with the presence of TiC, deteriorate some properties of Ti_2SnC. Purification of the Ti_2SnC powder is an unambiguous task. Systematic investigation of the influences of different parameters such as sintering atmosphere, starting mixtures as well as the ratios of starting composition on the high purity of the Ti_2SnC powder is necessary. To make clear the reason why the impurities are always present, it is also needed to understand the reaction mechanism of the formation of Ti_2SnC in the Ti–Sn–C system.

However, little information on systematically studying the influences of parameters, microstructures, and reaction mechanisms of Ti_2SnC was available until now. Although relative reaction mechanisms for the formation of Ti_2SnC were proposed by Vincent *et al.*[6] and Zhou *et al.*,[7] respectively, there are still some differences and unclear points. Furthermore, only two-dimensional Ti_2SnC platelets have been observed, while other shapes were not reported. According to the hexagonal structure of Ti_2SnC, it should possess different morphologies such as rod-like, plate-like, and equiaxed shapes, just like those for Ti_3SiC_2.[8]

In the present study, the main purposes are to fabricate the high purity of the Ti_2SnC powder from different mixture powders and to explain the reaction mechanism of the formation of Ti_2SnC from the microstructure observation and analysis results. A bimodal microstructure of Ti_2SnC is first reported, and its thermal stability in vacuum is also investigated.

II. Experimental Procedures

Commercial powders of Ti (−325 mesh, >99.2% purity), Sn (−200 mesh, >99.5% purity), C (graphite, −325 mesh, >99.0% purity), and TiC (average particle size: 4 μm, >98.0% purity) were used in the present study. All of the powders were from General Research Institute for Nonferrous Metals (GRINM), China.

Two types of powder mixtures containing Ti/Sn/C and Ti/Sn/TiC with different mole ratios were mixed in a polypropylene bottle for 10 h. The mixed powders were cold pressed to form compacts with a diameter of $\sim$20 mm and a height of $\sim$5 mm. The compacts were placed in a graphite crucible and then pressureless sintered at different temperatures for 1–6 h in a vacuum atmosphere. A differential scanning calorimetry (DSC) test on the powder of Ti/Sn/C was performed in a thermal analysis instrument (Netzsch STA409C, Selb, Germany) at a heating rate of 10°C/min, under flowing Ar in the temperature range of 25°–1250°C. The sintered samples were characterized by X-ray diffraction (XRD) using a D/Max 2200PC diffractometer (Japan) at 40 kV and 40 mA with Cu$K\alpha$ radiation. The microstructure of the sintered samples was observed by scanning electron microscopy (SEM, model: Hitachi S3500N, Japan, and Stereoscan 360, Cambridge, UK, respectively) equipped with energy-dispersive spectroscopy (EDS).

III. Results and Discussion

(1) Synthesis and Characterization of Ti_2SnC

Figure 1 shows the XRD patterns of the samples made of the Ti/Sn/C powders with a mole ratio of 2:1:1 (denoted as 2Ti–Sn–C) after sintering at different temperatures. The major peaks shown in Fig. 1(a) belong to Ti_2SnC, indicating that the Ti_2SnC phase should be formed below 1050°C. Ti–Sn compounds (Ti_6Sn_5 and Ti_5Sn_3) and Sn peaks can also be found in Fig. 1(a), however, with weak peaks. With increasing temperature in the range of 1050°–1200°C, the content of Ti_2SnC increases. At 1150°C, Ti_2SnC peaks are dominant, only with weak peaks of Sn (Fig. 1(b)). A pure Ti_2SnC powder was obtained at 1200°C (Fig. 1(c)). The present results, including the synthesis temperature and the powder purity, are different from those reported in

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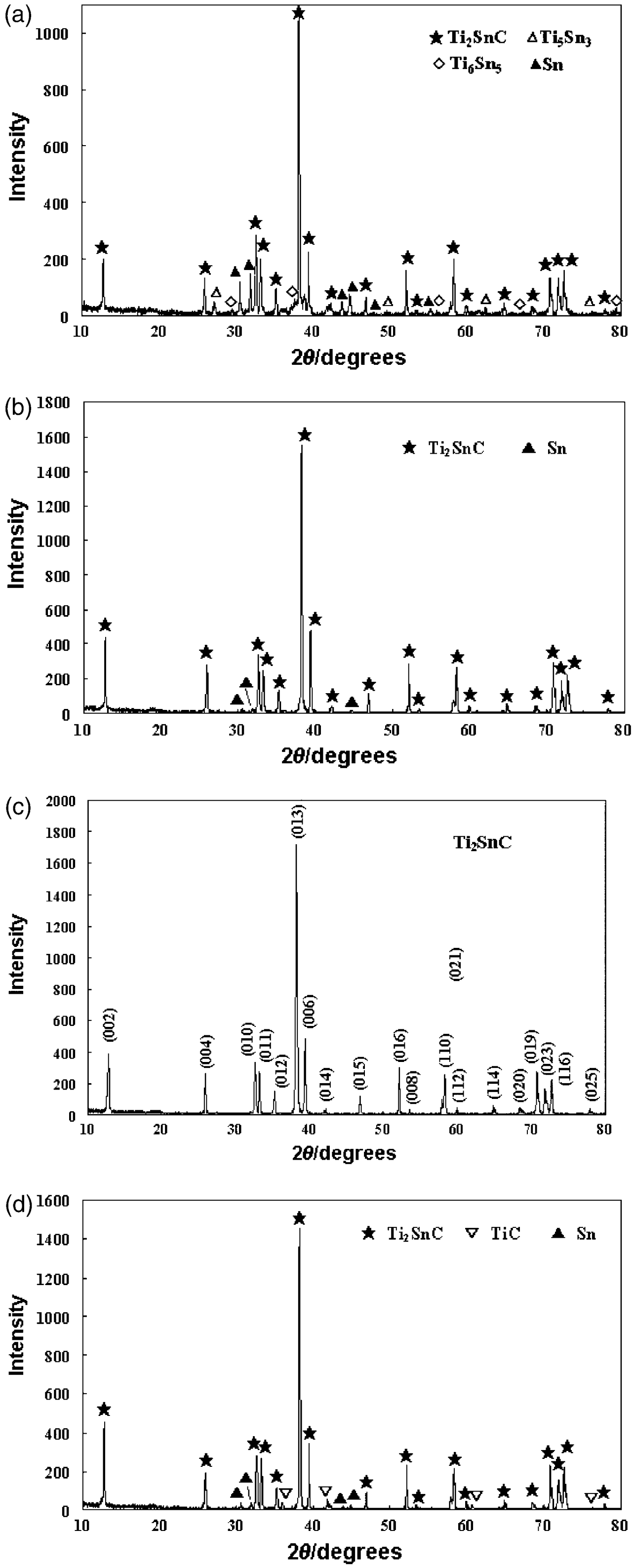

Fig. 1. X-ray diffraction patterns of the samples made of 2Ti–Sn–C powders after sintering at different temperatures for 1 h in a vacuum atmosphere, (a) 1050°C, (b) 1150°C, (c) 1200°C, and (d) 1250°C.

references.[3–7] One of the main reasons could be attributed to the sintering atmosphere, because the previously reported Ti_2SnC powders containing Sn or TiC were always synthesized by sintering a stoichiometric mixture of Ti/Sn/C in an Ar atmosphere.[3–7] We have also found that the Ti_2SnC powder was always contaminated by Sn and TiC after sintering the mixture of Ti/Sn/C in an Ar atmosphere in the range of 1050°–1200°C. So it confirmed that vacuum atmosphere improves the Ti_2SnC powder's purity.

Further increase in temperature results in a decrease in the content of Ti_2SnC. As the temperature increases to 1250°C for 1 h, TiC and Sn appear in the XRD pattern (Fig. 1(d)). The main reason is the decomposition of Ti_2SnC, which has been analyzed in the section on "Thermal Stability of Ti_2SnC in Vacuum Atmosphere." Figure 2 shows the morphologies of the sample after sintering at 1150°C. A few C particles identified by EDS (Fig. 3(a)) were found in the sample, shown in Figs. 2(a) and (b). However, these unreacted or residual C particles with a size less than 20 μm were not detected by XRD analysis (Fig. 1(a)), mainly owing to the lower amount that exceeds the limit of detection. Around the residual C particles, the Ti_2SnC grains with smooth surfaces cluster together. They have a growth tendency that is perpendicular to the surfaces of the C particles (Fig. 2(a)). From careful observations from Figs. 2(a) and (b), it can be seen that C particles are covered by a double layer containing an inner layer and an outer layer, which was analyzed by EDS, shown in Fig. 3. The inner layer is composed of TiC (Fig. 3(b)), which is thinner than 1 μm. The outer layer identified by EDS (Fig. 3(c)) is composed of Ti, Sn, and C and the atomic ratio of Ti/Sn is 2:1, indicating the Ti_2SnC phase.

Figure 4(a) shows the morphology of the Ti_2SnC grains taken from the fracture surface of the sample after sintering at 1200°C for 1 h. These plate-like grains are less than 8 μm in size, with thickness in the range of 0.3–1.3 μm. All of the grains exhibit a smooth surface, indicating that they grow and develop in the liquid.

However, another typical feature of the Ti_2SnC grains has been found on the surface at the same sample. A large amount of Ti_2SnC clusters with a rod-like shape and a smooth surface,

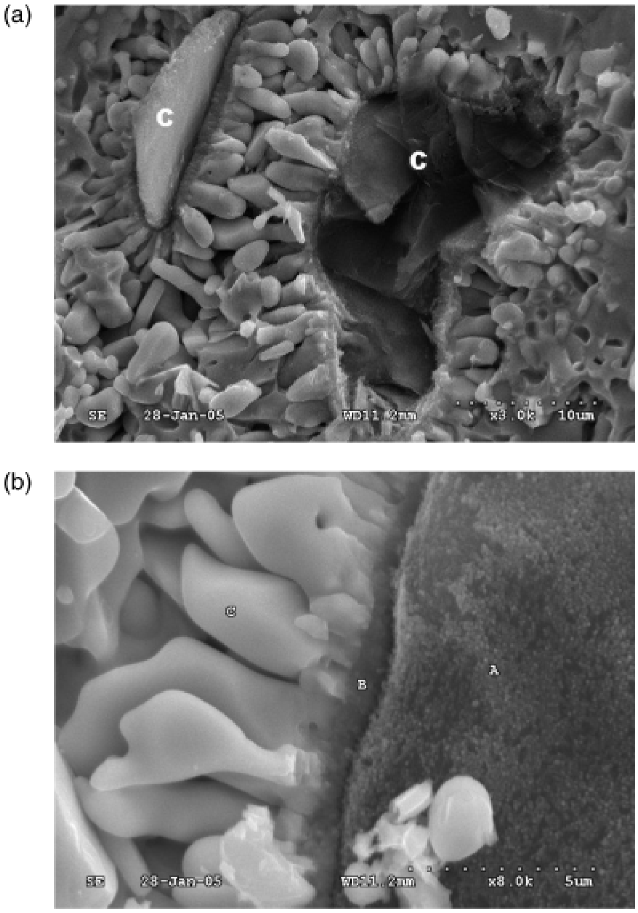

Fig. 2. Scanning electron micrographs of the fracture surfaces of the sample made of 2Ti–Sn–C powders after sintering at 1150°C for 1 h shown in (a) and (b). (a) A lower magnification micrograph; the marked "C" particles are graphite, and (b) a higher magnification micrograph.

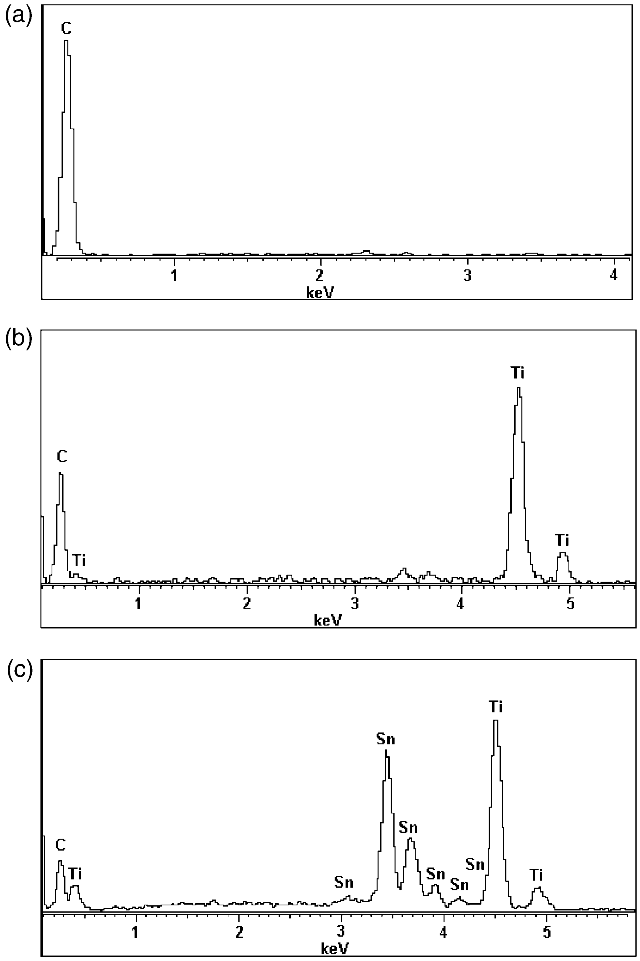

Fig. 3. Energy-dispersive spectroscopy spectra from the marked A, B, and C areas in Fig. 2(b) shown in (a), (b) and (c), respectively.

identified by EDS, is shown in Fig. 4(b). The rod-like grains cluster together densely and mainly grow toward the same orientation and its tip is round and smooth. These grains are ~10 μm in length and ~1 μm in diameter.

On carefully comparing the observations from Figs. 2 and 4, it can be deduced that the clusters must grow around the C particles. The shape of the Ti_2SnC particles shown in Fig. 4 is different, although taken from the same specimen, but not the same location. The difference mainly results from the growth environment and the size of the C particles. The images shown in Fig. 2 are taken from the inner area of the sample, in which the growth of the Ti_2SnC grains is restrained by adjacent particles. However, the Ti_2SnC grains at the outer surface will grow free from restriction, so these Ti_2SnC grains exhibit a long rod feature. From the above observations, it can be seen that Ti_2SnC has an anisotropic growth behavior, similar to 312 phases (Ti_3SiC_2, Ti_3AlC_2, etc.).

Furthermore, sufficient liquid phase benefits the rapid growth of Ti_2SnC, especially at the simple surfaces where sufficient liquid phase and minimum restriction both favor the Ti_2SnC grains to grow rapidly and develop a rod-like microstructure. This supposition was confirmed by additional evidence in which excess Sn in the Ti–Sn–C reaction system benefits the rapid growth of the Ti_2SnC rod grains. A starting composition with an extra 10% mol Sn (2Ti–1.1Sn–C) is used and sintered under the same condition as that for 2Ti–Sn—C. The results show that more Ti_2SnC rods appear both on the surface and in the inner area of the sample. Figure 5, taken from the inner area of sample, shows that Ti_2SnC rods ~10 μm in length are clustered around the residual C particles marked by arrows. The residual C particles are ~2 μm in size. The above-formed feature is discussed in the following section.

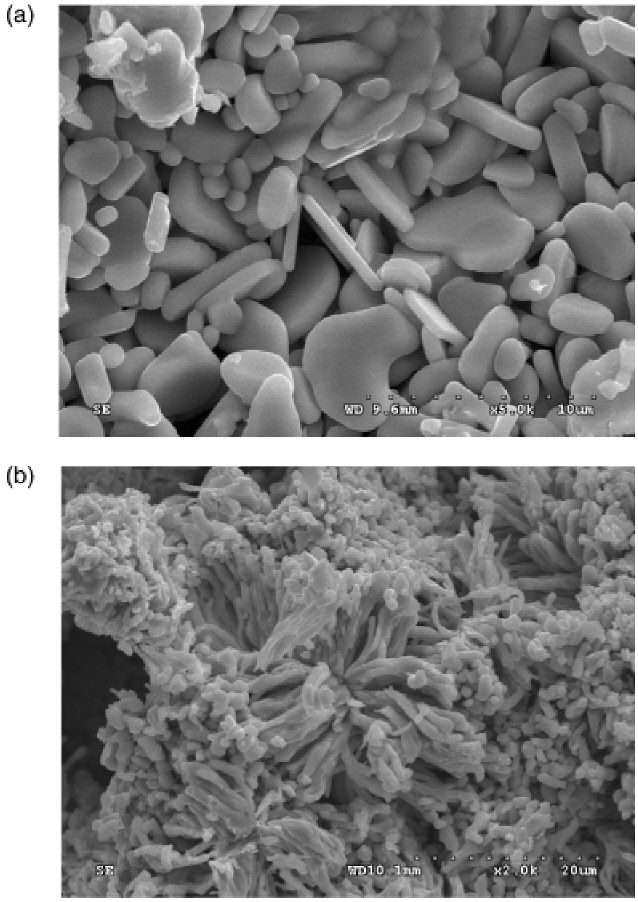

Fig. 4. Scanning electron micrographs for the sample made of 2Ti–Sn–C powders after sintering at 1200°C for 1 h. (a) Fracture surface, and (b) surface of the sample.

(2) Reaction Mechanism for Formation of Ti_2SnC

From the above observations, it is necessary to clarify the mechanism for the formation of Ti_2SnC.

Figure 6 shows the DSC curve of a stoichiometric mixture of Ti, Sn, and C powders. The sharp endothermic peak at 231°C was observed, corresponding to the melting of Sn. At 498°C, the first broad exothermic peak appeared, which should be attributed to a reaction between Ti and Sn to form Ti_6Sn_5. The second exothermic peak at 756°C was associated with a reaction between Ti and Ti_6Sn_5 to form Ti_5Sn_3. The above results have been further confirmed by XRD analysis (XRD patterns not

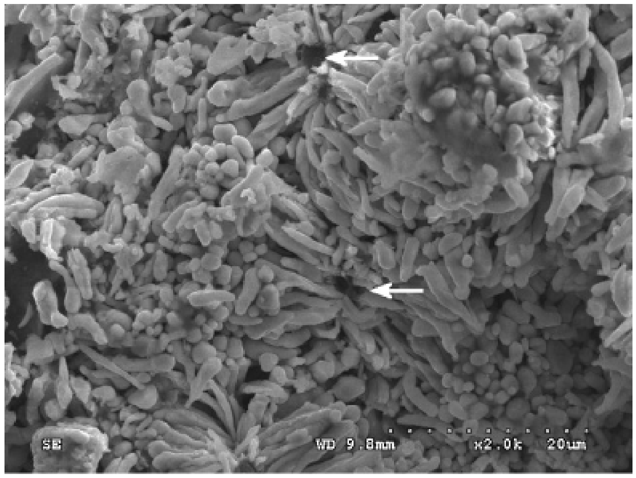

Fig. 5. Scanning electron micrograph of the fracture surface taken from the inner area of the sample made of 2Ti–1.1Sn–C and sintered at 1200°C for 1 h. Residual C particles are marked by white arrows.

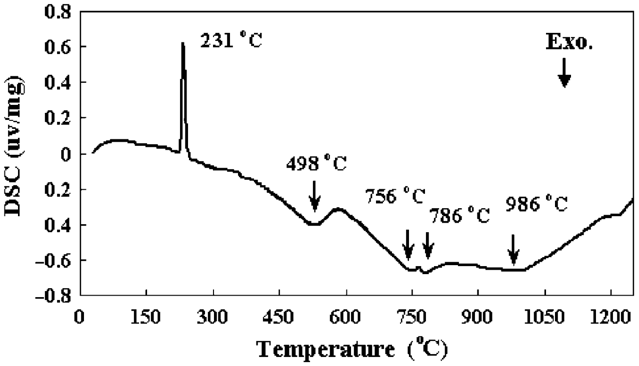

Fig. 6. Differential scanning calorimetry curve of a stoichiometric mixture of Ti, Sn, and C powders.

shown). Only a new phase of Ti_6Sn_5, except for Ti, Sn, and C peaks, was found in the XRD pattern after sintering the stoichiometric mixture of Ti/Sn/C powders at 500°C in an Ar atmosphere for 1 h, while both Ti_6Sn_5 and Ti_5Sn_3 were found at 730°C. The third exothermic peak at 786°C was related to the formation of TiC. The last exothermic peak with a broad and a weak shape around 986°C corresponded to the formation of Ti_2SnC from a reaction between Ti and Sn compounds (Ti_6Sn_5 and Ti_5Sn_3) and TiC.

Thus, the following reactions occur in an orderly manner during the sintering of the mixture of Ti, Sn, and C powders:

$$\mathrm{Sn}(s) \xrightarrow{\text{around } 232^\circ\mathrm{C}} \mathrm{Sn}(l) \tag{1}$$

$$5\mathrm{Sn}(l) + 6\mathrm{Ti}\,(s) \xrightarrow{\text{around } 498^\circ\mathrm{C}} \mathrm{Ti_6Sn_5}\,(s) \tag{2}$$

$$3\mathrm{Ti_6Sn_5}\,(s) + 7\mathrm{Ti}\,(s) \xrightarrow{\text{around } 756^\circ\mathrm{C}} 5\mathrm{Ti_5Sn_3}\,(s) \tag{3}$$

$$\mathrm{Ti}\,(s) + \mathrm{C}\,(s) \xrightarrow{\text{around } 786^\circ\mathrm{C}} \mathrm{TiC}\,(s) \tag{4}$$

$$\mathrm{Ti-Sn\,comp.}\,(s) + \mathrm{TiC}\,(s) \xrightarrow{\text{around } 986^\circ\mathrm{C}} \mathrm{Ti_2SnC}\,(s) \tag{5}$$

Based on the DSC, XRD, and SEM analyses, a model shown in Fig. 7 has been proposed to further explain the growth mechanism as follows:

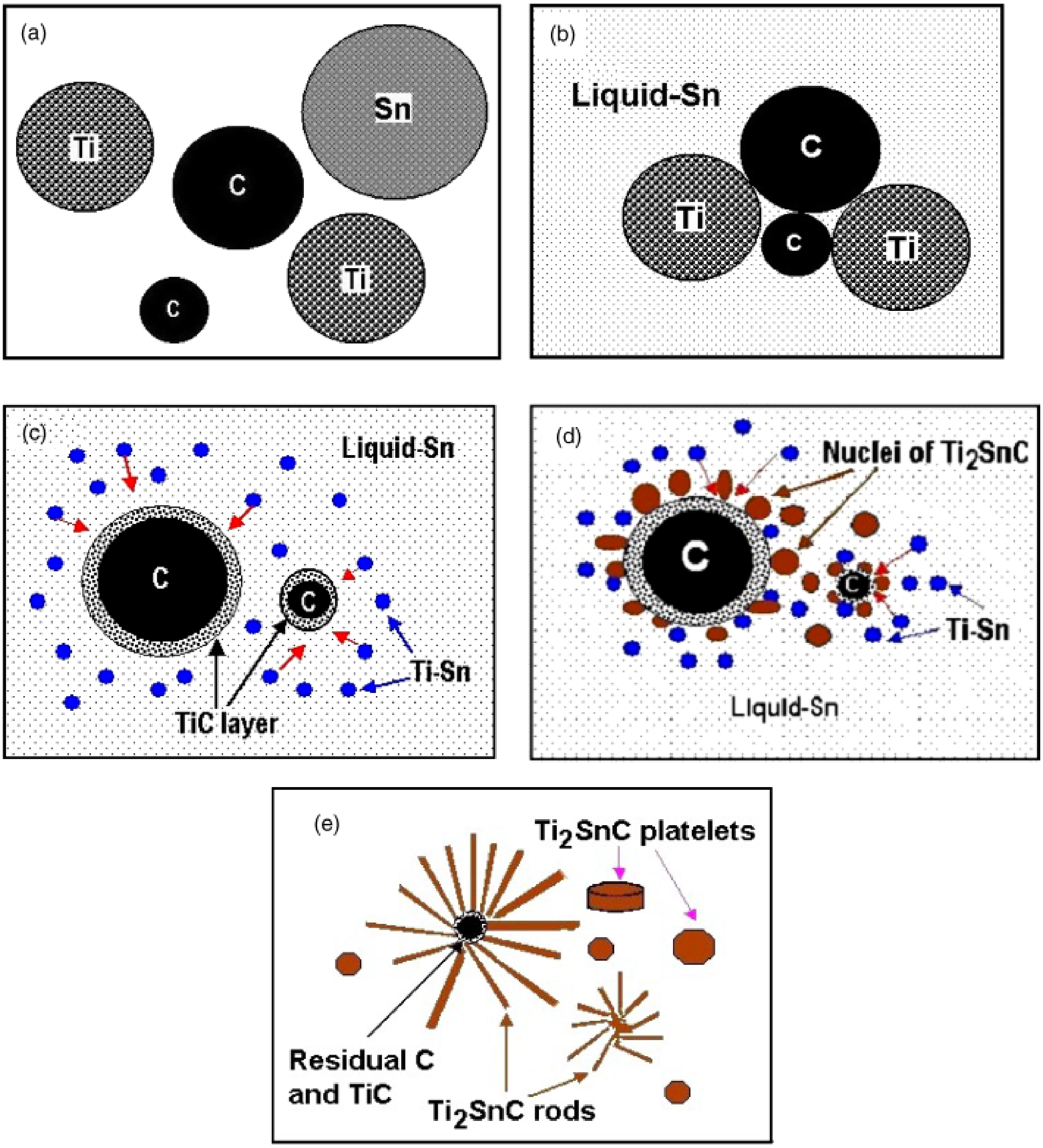

Fig. 7. Proposed growth mechanism for the formation of Ti_2SnC with a bimodal microstructure shown in (a)–(e).

At first stage, the powders of Ti, Sn, and C are mixed homogeneously (Fig. 7(a)). As the temperature increases to above Sn melting point (232°C), Sn starts to melt. With increasing temperature, molten Sn spreads everywhere; under this environment, Ti and C particles are easily rearranged and are close to each other (Fig. 7(b)). Ti atoms diffuse toward and accumulate in the grain boundaries of C that result in the formation of a thinner Ti–C layer (not TiC) owing to the strong chemical affinity of Ti to C. When the temperature increases to 500°C, Ti reacts with Sn to form Ti–Sn intermetallics, which includes four phases in the Ti–Sn binary system such as Ti_6Sn_5, Ti_5Sn_3, Ti_2Sn, and Ti_3Sn. However, the Ti_6Sn_5 compound was first formed according to XRD and DSC analyses. With increasing temperature, Ti continues to react with Ti_6Sn_5 to form Ti_5Sn_3. The reactions producing Ti_6Sn_5 and Ti_5Sn_3 are exothermic, which induces a reaction occurrence in the previously formed Ti–C layer. So the thin TiC layer forms around the C particles (Fig. 7(c)). On increasing the temperature to 980°C, a reaction producing Ti_2SnC takes place between the Ti–Sn compounds and TiC. Nuclei of Ti_2SnC precipitate and grow on the surface of the TiC layer (Fig. 7(d)). All of the above reactions are exothermic and may occur in the liquid-Sn system, in which Ti_2SnC grows fast and develops on the TiC layer.

With repetition of the above reactions, the smaller C particles are consumed quickly and nuclei of Ti_2SnC develop into platelets. Some medium-size C particles are consumed gradually, and the Ti_2SnC grains formed grow around the C particles until they are exhausted, leaving Ti_2SnC clusters (Fig. 7(e)). However, if the C particles were larger and other Ti–Sn compounds were consumed completely, the residual C cores would be left and covered with the inner layer of TiC and the outer layer of Ti_2SnC clusters, as shown in Fig. 7(e).

The effect of the C particle size on the microstructural features of Ti_2SnC has been confirmed by previous work in which mechanically alloyed Ti/Sn/C powders consisting of sub-micrometer or nano-sized C particles were used to synthesize Ti_2SnC.[9] It was found that the Ti_2SnC grains were platelet, not rod like, whether present on the surface or in the inner area of the sample.

The formation of the bimodal microstructure of Ti_2SnC has relation not only to the C particle size, liquid phase, and location but also to the grain growth rate, because crystal morphology is dependent on the grain growth rate in different planes. The slowly growing face plays an important role in determining the crystal morphology.[10] For the hexagonal crystal structure of Ti_2SnC, the crystal feature is determined by the relative growth rate on (101), (002), and (100) faces, just like Ti_3SiC_2.[8] If the growth rate on the (101) face is the fastest, the (002) and (100) faces exhibit a relatively slow growth rate, and the rod shape will be formed, as shown in Figs. 4(b) and 5. If the growth rate on the (100) face is the fastest, and the (002) and (101) faces have a relatively slow growth rate, the thin plate-like shape will be formed as shown in Fig. 4(a).

From the above observations and discussion, it is further confirmed that TiC plays an important role in the formation of Ti_2SnC, although Vincent *et al.*[5] deduced that TiC and a Sn–Ti alloy are in thermodynamic equilibrium. But in the present study, the reaction between TiC and the Ti–Sn compounds to form Ti_2SnC is unambiguous.

A further investigation for the formation of Ti_2SnC by sintering a mixture of Ti/Sn/TiC powders has been performed according to the following equation:

$$\mathrm{Ti} + \mathrm{Sn} + \mathrm{TiC} \rightarrow \mathrm{Ti_2SnC} \qquad (6)$$

A large amount of Ti_2SnC has been obtained by sintering the above mixture at 1200°C in a vacuum atmosphere, while a small amount of TiC and Sn as impurities accompanies Ti_2SnC. High purity of Ti_2SnC is obtained after sintering the mixture of Ti, Sn, and TiC with a mole ratio of 1:0.8:0.9 (Ti–0.8Sn–0.9TiC) at 1200°C for 15 min (Fig. 8). The Ti_2SnC grains obtained also possess a plate-like shape and are smaller than 4 μm in size. This result does confirm that Ti_2SnC forms between the Ti–Sn compounds and TiC. Furthermore, the rod-like feature of Ti_2SnC was not found in these specimens, further illustrating that the size of the C particles influences the microstructural feature of Ti_2SnC.

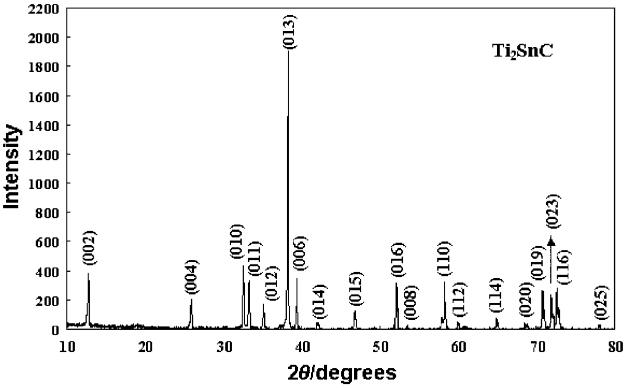

Fig. 8. X-ray diffraction pattern of the sample made of Ti–0.8Sn–0.9TiC and sintered at 1200°C for 15 min.

(3) Thermal Stability of Ti_2SnC in a Vacuum Atmosphere

Barsoum *et al.*[2] reported that Ti_2SnC might decompose at 1325°±25°C in an Ar atmosphere. Dong *et al.*[5] reported, according to DTA and TGA analyses, that the decomposition of Ti_2SnC was stable up to at least 1200°C in an Ar atmosphere. Confirming the decomposition temperature in a different atmosphere is of importance for Ti_2SnC in versatile applications.

However, in the present study, the decomposition temperature of Ti_2SnC in vacuum is 1250°C on the basis of the results given in Figs. 1 and 9.

As the holding time at 1250°C increased to 6 h, a large amount of TiC was formed and Sn also appeared in the XRD patterns (Fig. 9). But no Ti_2SnC was found, indicating that it has completely converted to the former two phases. In addition, a large amount of spherical Sn granules with metal luster and less than 3 mm in size were found on the walls of the graphite crucible. The main reason is that Sn evaporates from the sample at a high temperature and then condenses on the walls as the ambient temperature decreases. Hence, Ti_2SnC dissociates according to the following equation:

$$\mathrm{Ti_2SnC} \rightarrow \mathrm{Ti_2C} + \mathrm{Sn} \qquad (7)$$

Figure 10 shows the micrographs of the fracture surface of the sample made of 2Ti–1.1Sn–C and sintered at 1250°C for 4–6 h. Clusters with large sizes were found, and a large amount of TiC particles less than 3 μm in size agglomerated in the root of the

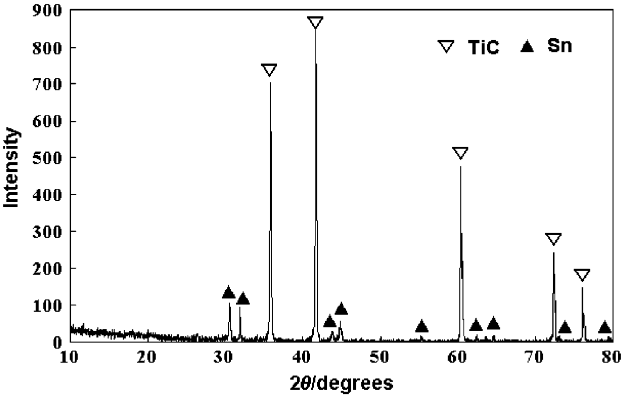

Fig. 9. X-ray diffraction pattern of the sample made of 2Ti–Sn–C powders after sintering at 1250°C for 6 h.

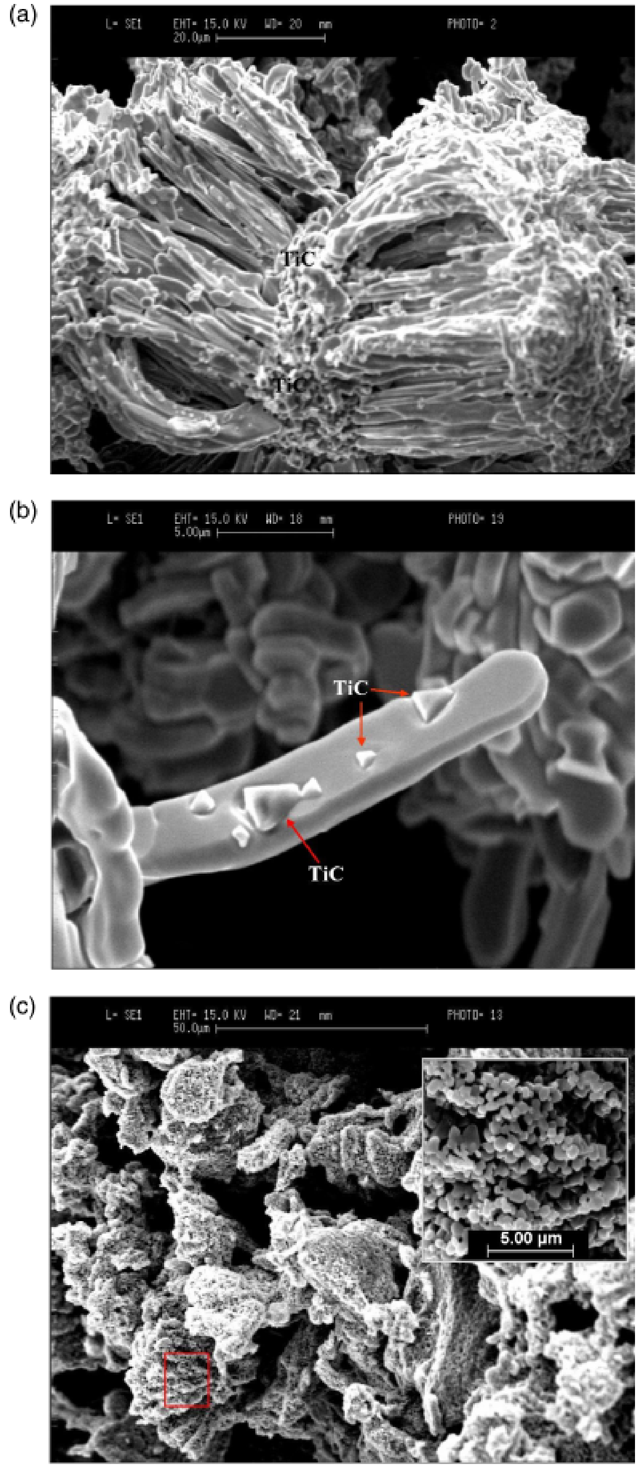

Fig. 10. Scanning electron micrographs of the fracture surface of the sample made of 2Ti–1.1Sn–C and sintered at 1250°C for 4 h shown in (a) and (b), and for 6 h shown in (c). (a) Elongated Ti_2SnC laths and smaller TiC particles, (b) triangle structure of TiC formed on an elongated Ti_2SnC lath. (c) Microstructure of the decomposed sample. The inset shows an enlarged micrograph taken from the marked area in (c).

clusters, as shown in Fig. 10(a). However, the Ti_2SnC rods grew larger than 80 µm in length, indicating that the size of Ti_2SnC increases with an increase in both temperature and holding time. Careful observation shows that the previously formed rods have developed an elongated lath shape (Figs. 10(a) and (b)). Some TiC particles that resulted from the decomposition of Ti_2SnC with a triangle shape were embedded in the surface of the lath (Fig. 10(b)). However, as the holding time was up to 6 h at 1250°C, all of the Ti_2SnC grains converted into TiC (Fig. 10(c)). It can be clearly seen from the inset in Fig. 10(c) that the TiC particles formed are of a homogeneous size of about 0.8 µm.

To understand properly the conversion of Ti_2SnC to TiC and Sn, it is necessary to analyze the crystal structure of Ti_2SnC, which consists of layers of Sn atoms connected with octahedral Ti_6C. In the layered structure, each Sn atom links two chains formed by Ti–C–Ti atoms with a covalent bond. The bonding in the Ti–C–Ti bond chain is strong, while that linking the Ti–C–Ti chain and Sn atom is relatively weak.[11] So at the decomposition temperature, Sn atoms easily diffuse from Ti_2SnC, leaving Ti_2C block layers that finally form a $TiCx$ structure with ordered C vacancies, which is similar to the decomposition of Ti_3SiC_2.[12]

It has been proved that "A" element in the $M_{n+1}AX_n$ compound is easily induced to diffuse outward from the layered structure under certain conditions, for example, when Ti_3SiC_2 was placed in an environment such as cryolite,[12] chlorine,[13] or molten Al,[14] in which the Si atoms were induced to migrate outward, leaving the $TiCx$ layers behind. Additional evidence also confirmed that Ti_3AlC_2 decomposed at 1450°C with Al diffusion outward, with the formation of larger TiC particles, which exhibit a polyhedral shape or a layered feature.[15]

IV. Conclusion

High-purity Ti_2SnC powder has been obtained from mixtures of Ti/Sn/C with a mole ratio of 2:1:1 and Ti/Sn/TiC with 1:0.8:0.9 after pressureless sintering at 1200°C in vacuum for 1 h and 15 min, respectively. Ti_2SnC with a bimodal microstructure of plate-like and rod-like shapes appeared in the samples after pressureless sintering the Ti/Sn/C mixture. The bimodal microstructure mainly resulted from the C particle size, growth environment, and the grain growth on the different planes. In addition, liquid Sn content also plays an important role in the above microstructure formation. The mechanism for the formation of Ti_2SnC was analyzed and a reaction model for explaining the mechanism was proposed. With increasing temperature, Sn melted and formed a liquid environment and particle rearrangement occurred. Ti atoms diffuse toward the surfaces of C particles, around which a thin Ti–C layer forms due to the strong chemical affinity of Ti to C. With increasing temperature, Ti and Sn first react to form Ti–Sn intermetallic compounds, and then, TiC forms in the Ti–C layer. Lastly, Ti_2SnC forms from a reaction between the Ti–Sn compounds and TiC at a certain temperature. The last reaction to form Ti_2SnC has been further proved by sintering Ti/Sn/TiC powders at 1200°C.

The thermal stability of Ti_2SnC is lower than 1250°C in vacuum. Above 1250°C, Ti_2SnC decomposes to TiC and Sn. Analyzing the crystal structure can lead to a proper understanding of the decomposition of Ti_2SnC. At a high temperature, Sn easily diffuses outward from the weak links between Sn and the Ti–C–Ti chains, leaving Ti_2C block layers that finally formed a $TiCx$ structure with ordered C vacancies.

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