

# Synthesis of $Ti_3GeC_2$ Powders from Ti-Ge-TiC Mixtures by Pressureless Sintering

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## Research Article

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# Abstract

Ti<sub>3</sub>GeC<sub>2</sub> compound has excellent electrical and mechanical properties, which can be used as a potential reinforcement for Ag-based electrical contact materials. However, few reports have been addressed on the synthesis of its powders. The present study, therefore, presents a new route to fabricate high-purity Ti<sub>3</sub>GeC<sub>2</sub> powders from Ti/Ge/TiC by pressureless sintering in vacuum. The influence of sintering temperature and Ge content on the powder purity was studied and the optimized conditions are found to be 1550 °C and Ti:Ge:TiC=1:1.1:2. In addition, the reaction path of Ti/Ge/TiC was revealed to be three steps: First, liquid Ge starts to react with Ti to form Ti<sub>5</sub>Ge<sub>3</sub> compounds at around 1140 °C; Then Ti<sub>5</sub>Ge<sub>3</sub> consumes the liquid Ge and TiC to form Ti<sub>2</sub>GeC at around 1200 °C; Finally, Ti<sub>2</sub>GeC transfers into Ti<sub>3</sub>GeC<sub>2</sub> with the consumption of residual TiC. The present study lays the foundation for the subsequent applications of Ti<sub>3</sub>GeC<sub>2</sub> powders in high performance composites.

## 1. Introduction

MAX phases, with the formula of M<sub>n+1</sub>AX<sub>n</sub>, where n = 1 ~ 3, M is an early transition metal, A is an A-group (mostly IIIA and IV A) element, and X is carbon or nitrogen, are a series of layered ternary carbides or nitrides[1, 2]. They were first reported by Jeitschko and Nowotny in the early 1960s [3]and initially named in 2000 by Barsoum[4]. The unique crystal structure and combined bonding of MAX phases endow them with both metal and ceramic characteristics, such as excellent electrical and thermal conductivities, even exceeding the corresponding transition metal elements[5, 6]. Accordingly, MAX phase materials have broad application prospects, including high-temperature structural materials, machinable ceramics, kiln furniture, wear and corrosion protection, heat exchangers, rotating parts etc[4, 7].

As a typical MAX phase, Ti<sub>3</sub>GeC<sub>2</sub> has a theoretical density of 5.55 g/cm<sup>3</sup> and a hexagonal crystal structure[8, 9]. Ti<sub>3</sub>GeC<sub>2</sub> exhibits moderate hardness (2 ~ 6 GPa), high Young's modulus (~ 197 GPa), excellent machinability, high yield strength, and significant plasticity at 1300 °C[7, 10]. It also shows excellent corrosion and oxidation resistance, remarkable thermal shock resistance, sound electrical and thermal conductivity[10, 11]. Wolfsgruber et al. first fabricated bulk Ti<sub>3</sub>GeC<sub>2</sub>[8] in 1967 by hot pressing at 1200 °C for 20 h from Ti, Ge, and C powder mixtures. In 1997, Barsoum et al.[7] synthesized Ti<sub>3</sub>GeC<sub>2</sub> plates by hot pressing at 1500 °C for 4 h. However, the phase purity was not satisfied due to the high content of carbide impurities, which was attributed to the severe loss of Ge during sintering. To compensate for the loss of Ge, Kephart, et al. [12]added an excess of Ge in the starting materials during the preparation of Ti<sub>3</sub>GeC<sub>2</sub> bulks by an arc melting ingot method, while several impurity phases like TiC, Ti<sub>5</sub>Ge<sub>3</sub>, and Ti<sub>2</sub>GeC were formed. To further improve the purity of Ti<sub>3</sub>GeC<sub>2</sub>, the same authors heated the reactants at 1200 °C for about 100 hours[12], but a large amount of TiC, unreacted Ge, and other Ti-Ge intermetallic compounds were still detected. Barsoum et al. [13]synthesized the bulk Ti<sub>3</sub>GeC<sub>2</sub> and Ti<sub>3</sub>(Si<sub>x</sub>Ge<sub>1-x</sub>)C<sub>2</sub> (x = 0.5, 0.75) solid solutions by hot isostatic pressing (HIP) in 2004. However, these samples still contains a large amount of binary carbides unexpected.

Since the first preparation of  $Ti_3GeC_2$  in 1967, most studies focused on the synthesis of its bulk samples, but few reports concerned the direct production of  $Ti_3GeC_2$  powders. Rahul et al. [14] synthesized  $Ti_3GeC_2$  powder via pressureless sintering at 1500 °C, containing  $Ti_5Ge_3$  and TiC impurities. Generally, the  $Ti_3GeC_2$  powders was fabricated from Ti/Ge/C raw materials[14], similar to the preparation of bulk samples[7, 8, 12, 13]. The motivation to further improve  $Ti_3GeC_2$  powder purity was inspired by the report that using Ti/Si/TiC instead of Ti/Si/C powder mixtures will significantly increase the phase purity of  $Ti_3SiC_2$  [15]. The synthesis of high-purity MAX phase powders will benefit to the production of MAX components with complicated structures via ceramic processing like slip casting, and also the development of MAX-reinforced composites. For instance, MAX phase can be used as the reinforcements for metal-based electrical contacts[16–21], where the synthesis of high-purity MAX powder is the prerequisite for the developments of high-performance Ag-MAX composites.

In the present paper, therefore,  $Ti_3GeC_2$  powders were prepared by pressureless sintering using Ti, Ge, and TiC as raw materials, and the processing parameters were optimized to improve the phase purity. Differential scanning calorimetry and X-ray diffraction analysis were applied to identify the formation mechanism.

## 2. Experimental Procedures

Powders of Ti (99.99%, ~ 45  $\mu m$ ), Ge(99.999%, ~ 75  $\mu m$ ), and TiC(99.95%, ~ 30  $\mu m$ ) were used as raw materials in this study. Ti/Ge/TiC powders with different molar ratios (1:0.9:2, 1:1:2, and 1:1.1:2) were mixed by Turbula mixer (T2F, Switzerland) for 24 h. These homogeneous mixtures were then respectively placed in Tungsten crucible and sintered at 1500–1550 °C at 10 °C/min for 2 h in a high-temperature vacuum furnace (~  $10^{-4}$  bar). Based on the preliminary experiments, the processing parameters such as temperature and composition were optimized. To determine the reaction route, differential scanning calorimetry (DSC, Netzsch 404C, Germany) was conducted on a 1Ti/1Ge/2TiC powder mixture under the Ar atmosphere at a scanning rate of 10°C/min. The phase constituents of  $Ti_3GeC_2$  powders were determined by X-ray diffraction (XRD, Bruker-AXS D8, Germany) with Cu K $\alpha$  radiation at a scanning step of 0.05° and scanning rate of 5°/min. Besides, The morphologies and chemical compositions of the synthesized  $Ti_3GeC_2$  powders were characterized by a scanning electron microscope (SEM, FEI/Philips Sirion 2000, Netherlands) equipped with an energy dispersive spectrometer (EDS, Aztecs X-MAX 80).

## 3. Results And Discussion

### 3.1. Effect of temperature on the formation of $Ti_3GeC_2$

To eliminate these impurity phases, the sintering temperature of  $Ti_3GeC_2$  powders was examined from 1500 °C to 1550°C. Figure 1a shows the XRD results of 1Ti/1Ge/2TiC powder sintered in vacuum for 2 h at different temperatures. At 1500 °C, the main phase of  $Ti_3GeC_2$  has been formed, but significant amount of TiC remains in the product, which is attributed to the relatively low reaction temperature and

thus the residual TiC unreacted. With the increase of temperature to 1550 °C, the content of  $Ti_3GeC_2$  in the product continues to increase, and the content of TiC decreases significantly if compared with 1500 °C. Therefore, the  $Ti_3GeC_2$  sintered from 1Ti/1Ge/2TiC powder mixture at 1550 °C has relatively high phase purity.

For comparison, Fig. 1b presents the XRD results of 3Ti/1Ge/2C powder mixtures sintered in vacuum for 2 h at 1500 °C and 1550 °C. Accordingly, the large amount of residual TiC at 1500°C and the gradually increased phase purity of  $Ti_3GeC_2$  at 1550 °C in the product sintered from 3Ti/1Ge/2C powder mixtures can be derived. These results are consistent with the literature. However, if compared with 1Ti/1Ge/2TiC specimens, the 3Ti/1Ge/2C ones produce higher TiC content in final products at the same sintering temperature according to the stronger peak intensity of TiC at 41.7°, which means the relatively lower phase purity. Therefore, Ti/Ge/TiC powder mixtures were utilized as starting materials to synthesize  $Ti_3GeC_2$  powder in the following experiments.

### 3.2. Effect of Ge molar ratio on the formation of $Ti_3GeC_2$

In addition to sintering temperature, the composition of raw materials also affects the phase purity of  $Ti_3GeC_2$  powder. 1Ti/xGe/2TiC powder mixtures with different Ge contents were sintered at 1550 °C for 2 h to fabricate  $Ti_3GeC_2$  powders. They were labeled as S1 (1Ti/0.9Ge/2TiC), S2 (1Ti/1.0Ge/2TiC) and S3 (1Ti/1.1Ge/2TiC), respectively.

As shown in Fig. 2, the S1 sample consists of the main phase  $Ti_3GeC_2$ , with a small amount of TiC and  $Ti_2GeC$  detected. When the content of Ge increases to 1.0 in the S2 sample, the amount of  $Ti_3GeC_2$  increases and those of TiC and  $Ti_2GeC$  decrease accordingly. With the further increase of Ge content to 1.1 in S3 sample,  $Ti_3GeC_2$  dominates the phase constituents with trace  $Ti_2GeC$  and TiC.

The Ge element exists as a liquid phase and promotes the formation of  $Ti_3GeC_2$  phase during the sintering process. When the content of Ge is less than the stoichiometric value of 1.0, the liquid Ge phase may become insufficient due to the evaporation loss at high temperatures during the sintering of Ti/Ge/TiC mixtures. Therefore, raw materials like TiC are left in the final product. Meanwhile, a small amount of  $Ti_2GeC$  as an intermediate phase is remained, as shown in S1 and S2 samples. When the content of Ge element reaches 1.1, the excessive Ge compensates its loss, accompanying with the mostly consumed TiC and the promoted transformation from  $Ti_2GeC$  to  $Ti_3GeC_2$ , as shown in S3 sample.

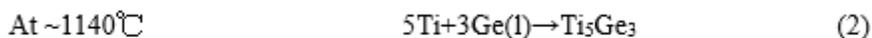
Figures 3(a)-(c) present the respective morphologies of the synthesized powders of S1, S2, and S3 samples, all of which have the typically layered structures of MAX phases. EDS patterns suggest the presence of Ti, Ge and C elements and the Ti/Ge ratios change slightly from 3.18–3.28, indicating the high purity of  $Ti_3GeC_2$  powders. The content of Ge in raw materials seems hardly to affect the microstructure of  $Ti_3GeC_2$  powders. Therefore, the synthesized conditions of  $Ti_3GeC_2$  powders are optimized to be the starting materials of 1Ti/1.1Ge/2TiC sintered at 1550 °C for 2 h.

### 3.3 Powder Synthesis

Figure 4 displays the DSC curve of 1Ti/1Ge/2TiC powder mixture heated from room temperature to 1350°C at a rate of 10°C/min. There is a sharp endothermic peak near 942°C, which corresponds to the melting of Ge. The formation of liquid Ge benefits to the diffusion and reaction among the raw materials. The broad exothermic peak appears at 1140–1200°C, suggesting some chemical reactions take place within this temperature range.

To determine the chemical reactions and phase changes of the raw materials during the heating process, 1Ti/1Ge/2TiC powders were respectively sintered at 1140 °C, 1200 °C and 1250 °C for 2 h, which corresponds to the starting, the ending and a higher temperatures to the exothermic peak. Figure 5 shows the XRD patterns of three samples sintered at these temperatures.

As sintered at 1140 °C, the sample is composed of a large amount of  $Ti_5Ge_3$  with a significant amount of Ge and TiC raw materials, as well as a small amount of  $Ti_2GeC$ . This indicates that the reaction between Ti and liquid Ge to form  $Ti_5Ge_3$  contributes mainly the appearance of exothermic peak at the starting temperature. For the sample sintered at 1200 °C, most of the peaks can be indexed to  $Ti_2GeC$  phase with a small amount of TiC and a trace of  $Ti_5Ge_3$  and residual Ge. With the increase of sintering temperature,  $Ti_5Ge_3$  reacts with Ge and TiC to form  $Ti_2GeC$ , which explains the exothermic peak around the ending temperature. Note that these results provide a ready method to fabricate high-purity  $Ti_2GeC$  powders. At temperatures higher than the exothermic peak,  $Ti_3GeC_2$  phase appears with the decreasing amount of  $Ti_2GeC$  and TiC, indicating the formation of  $Ti_3GeC_2$  with the consumption of  $Ti_2GeC$  and TiC. Therefore, the reaction route of  $Ti_3GeC_2$  from Ti/Ge/TiC powder mixtures can be described as follows:



### 4. Conclusions

The present study provides a new route to fabricate high-purity  $Ti_3GeC_2$  powders from Ti/Ge/TiC by pressureless sintering in vacuum. The influence of sintering temperature and Ge content on the  $Ti_3GeC_2$  powder purity and the corresponding reaction route was investigated. The main conclusions are as follows:

1. High-purity  $\text{Ti}_3\text{GeC}_2$  powders were successfully synthesized by pressureless sintering from the starting powder mixture of 1Ti/1.1Ge/2TiC at 1550 °C for 2 h. The purity of  $\text{Ti}_3\text{GeC}_2$  samples is mainly related to the sintering temperature and the Ge content in starting composition.
2. The reaction route of Ti/Ge/TiC power mixtures to  $\text{Ti}_3\text{GeC}_2$  was revealed to be three steps: First, Ge melts at 942 °C and starts to react with Ti to form  $\text{Ti}_5\text{Ge}_3$  at 1140 °C; Then,  $\text{Ti}_2\text{GeC}$  phase is completely formed by consuming  $\text{Ti}_5\text{Ge}_3$ , Ge and TiC at 1200 °C; finally,  $\text{Ti}_2\text{GeC}$  reacts with residual TiC to form  $\text{Ti}_3\text{GeC}_2$  gradually at higher temperatures.

## Declarations

## Acknowledgments

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## Figures

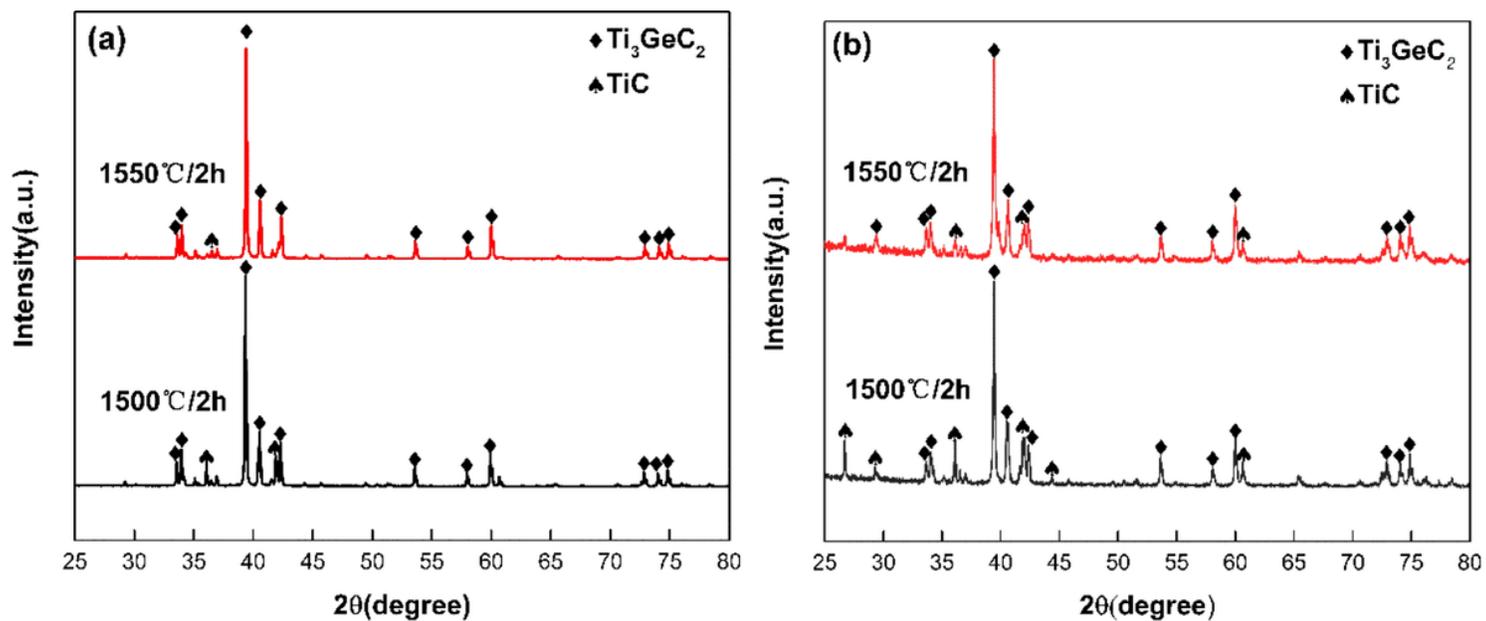


Figure 1

XRD patterns of (a) 1Ti/1Ge/2TiC and (b) 3Ti/1Ge/2C powder mixtures sintered at different temperatures for 2h.

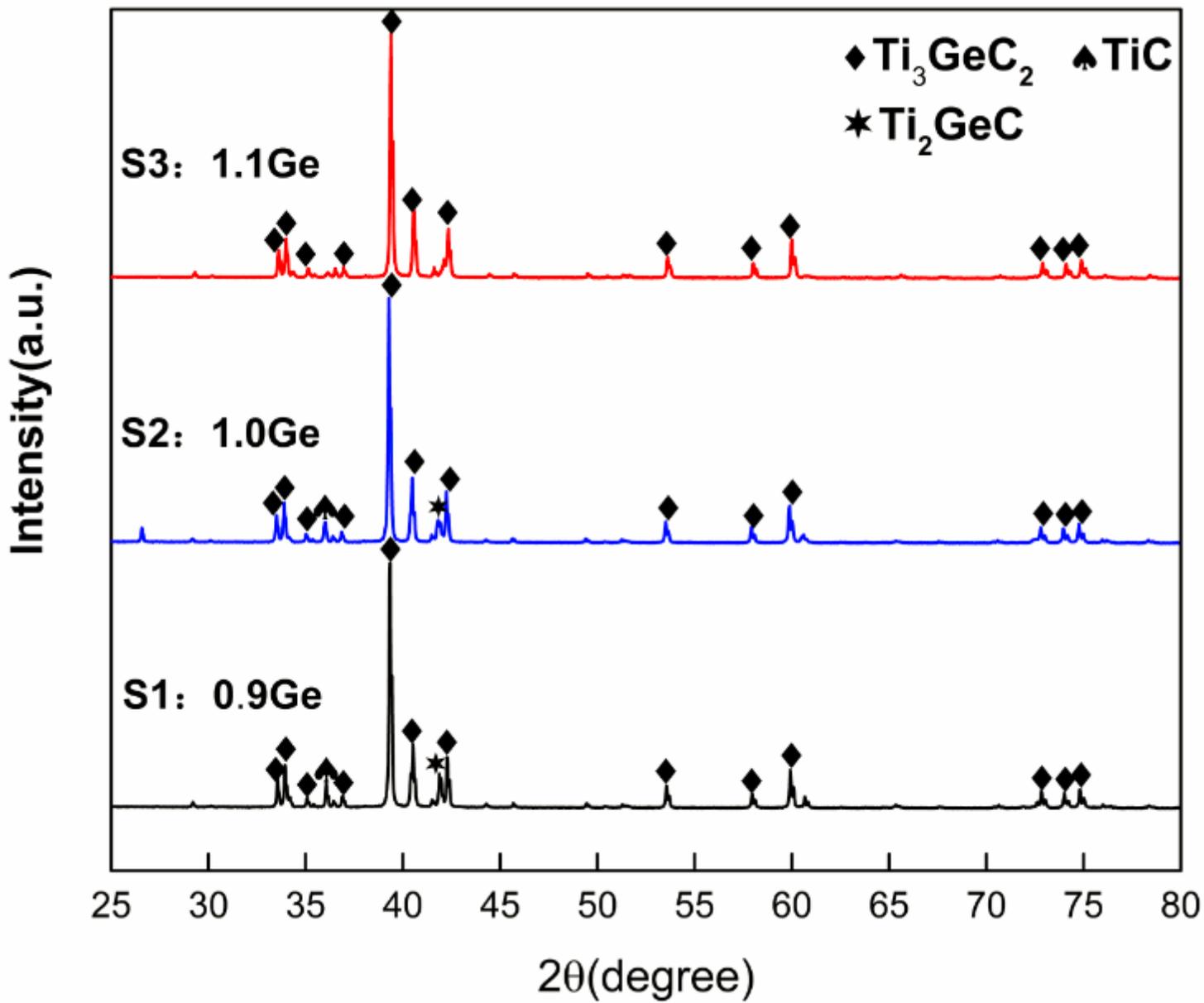
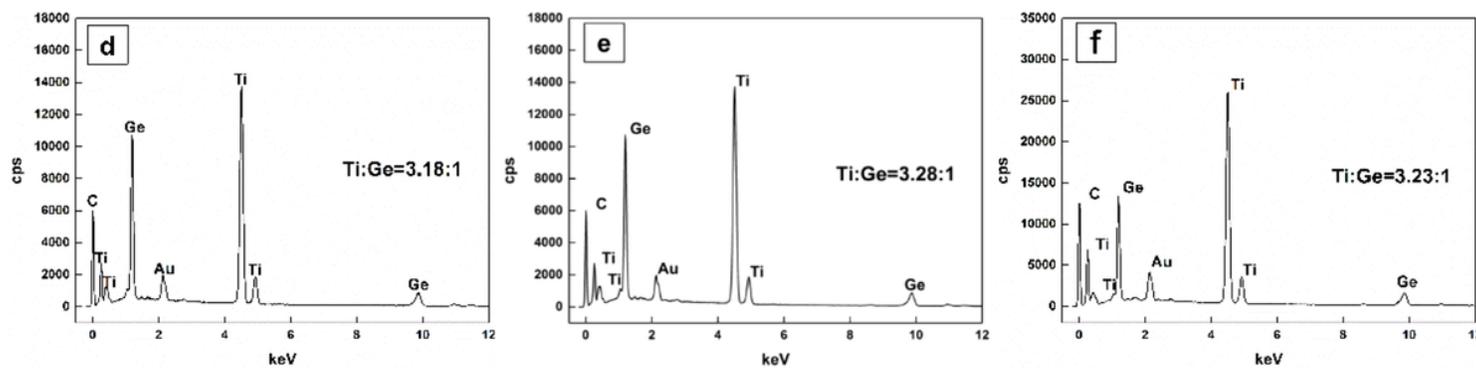
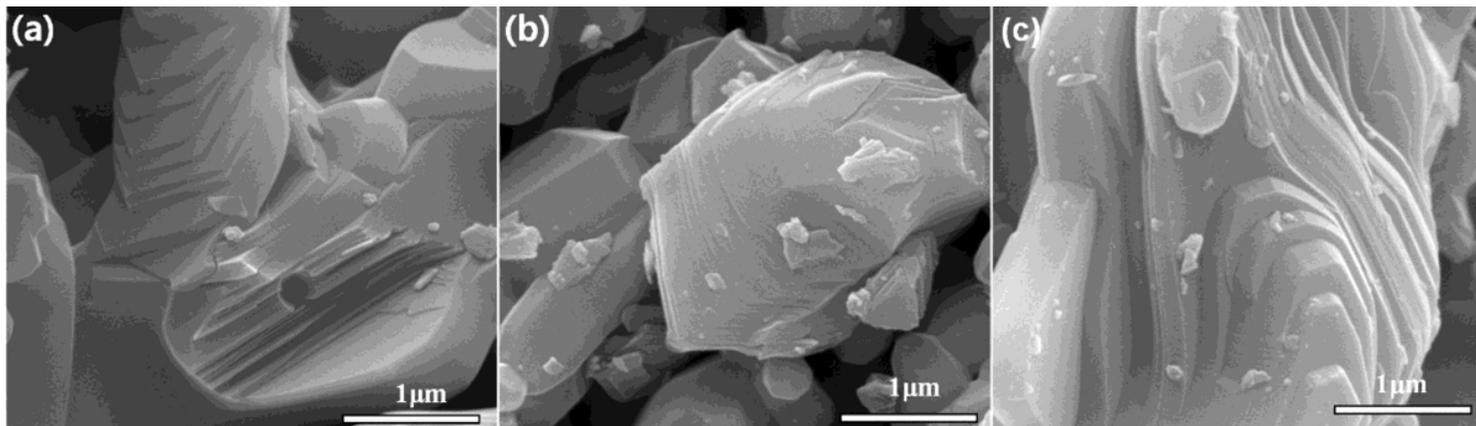


Figure 2

XRD patterns of 1Ti/xGe/2TiC powder mixtures with different Ge contents sintered at 1550 °C for 2 h



**Figure 3**

Typical morphologies of Ti<sub>3</sub>GeC<sub>2</sub> in the synthesized powders. (a) sample S1;(b) sample S2; (c) sample S3

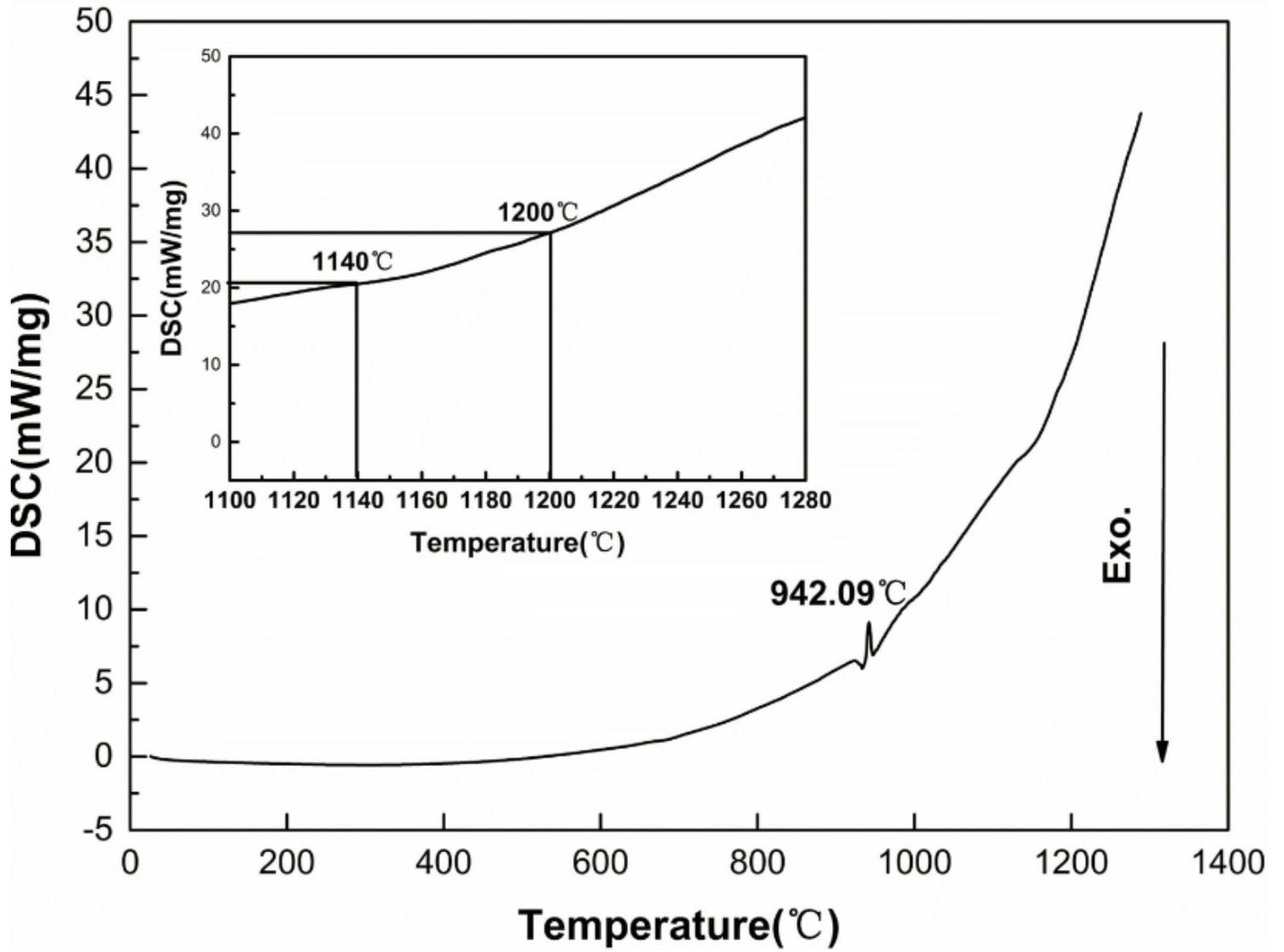


Figure 4

DSC curve of 1Ti/1.1Ge/2TiC powder heated to 1350 °C at 10 °C/min.

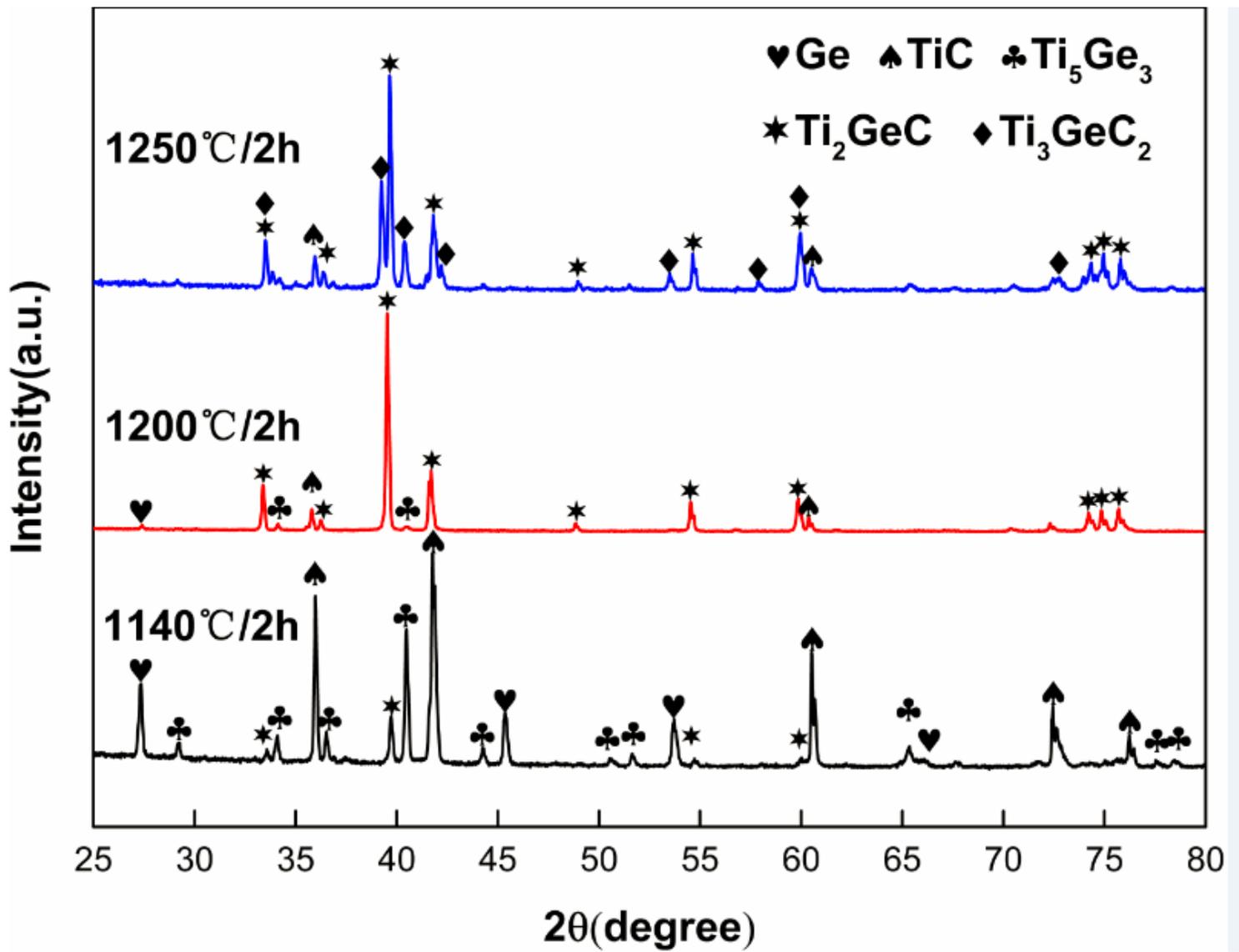


Figure 5

XRD patterns of 1Ti/1Ge/2TiC powder mixtures sintered from 1140 °C to 1250°C.