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Synthesis of High Pure Ti_3AlC_2 and Ti_2AlC Powders from TiH_2 Powders as Ti Source by Tube Furnace

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Abstract: Titanium aluminum carbide (Ti_3AlC_2 and Ti_2AlC) powders were synthesized from TiH_2 powders instead of Ti powders as Ti source by a tube furnace under argon atmosphere without preliminary dehydrogenation. 95 wt% pure Ti_3AlC_2 powders were synthesized from TiH_2/1.1Al/2TiC at 1 450 ℃ for 120 min. High-purity Ti_2AlC powders were also prepared from 3TiH_2/1.5Al/C and 2TiH_2/1.5Al/TiC powders at 1 400 ℃ for 120 min. The as-synthesized samples were porous and easy to be ground into powders. Sn or Si additives in starting materials increased the purity of synthesized Ti_3AlC_2 obviously and expanded the temperature range for the synthesis of Ti_3AlC_2. With Si or Sn as additives, high pure Ti_3AlC_2 was synthesized at 1 200 ℃ for 60 min from TiH_2/*x* Si/Al/2TiC and TiH_2/*x* Sn/Al/2TiC (x = 0.1, 0.2), respectively.

Key words: Ti_3AlC_2; Ti_2AlC; TiH_2; Sn; Si

1 Introduction

Ternary compound Ti_3AlC_2, which is isotypic with Ti_3SiC_2, exhibits a surprising combination of excellent properties of ceramics and metals. It is relatively soft (Vickers hardness of about 3.5 GPa) and elastically stiff (Young's modulus of 297 GPa and shear modulus of 124 GPa)[1]; it is lightweight (density of 4.2 g/cm^3) and easily machinable; and it has high thermal and electrical conductivity[2]. It has high compressive strength at both room and high temperature. Its failure mode is shear fracture below 1 000 ℃, while the deformation is ductile above 1 050 ℃[3]. Meanwhile, Ti_3AlC_2 has excellent oxidation resistance by forming adhesive continuous Al_2O_3 layer on Ti_3AlC_2 surface at high temperature[3].

In 1994, Pietzka and Schuster firstly reported the synthesis of Ti_3AlC_2 by sintering cold-compacted powder mixtures of titanium, TiAlx, Al_4C_3, and carbon at 1 300 ℃ in H_2 atmosphere for 20 h[4]. The purity of Ti_3AlC_2 was not reported[4]. Tzeonov and Barsoum prepared bulk polycrystalline Ti_3AlC_2 by reactive hot isostatically pressing (HIP) a mixture of titanium, graphite, and Al_4C_3 powders at 1 400 ℃ for 16 h. The purity of Ti_3AlC_2 was about 95 wt%[1]. In recent years, many kinds of methods had been used to synthesize Ti_3AlC_2 powders, bulks or films. Most widely used combinations for starting materials included Ti/Al/C[5, 6], Ti/Al/TiC[6-8], Ti/Al/C/TiC[9], TiH_2/Al/TiC[10], and TiH_2/Al/C[11].

Most methods employed metallic Ti powders as Ti source. Ti powders are expensive and result high cost of Ti_3AlC_2. TiH_2 powders are the intermediate products to make metallic Ti powders and cheaper than Ti powders. The price of commercial TiH_2 powders is 10% lower than that of Ti powders with an equivalent particle size[10,11]. Nevertheless, if TiH_2 powders are used to fabricate Ti_3AlC_2, long annealing time is essential for preliminarily removing hydrogen in TiH_2[12]. In addition, that dehydrogenating process causes many pores in as-synthesized products. Assistant pressure during sintering is needed to densify samples[10,11]. The cost increasing due to expensive processing balances out the cost decreasing because of cheaper raw materials. On the other hand, if the powders of Ti_3AlC_2 or Ti_2AlC rather than dense bulks are desired, the costly sintering process such as hot pressing or pulse discharge sintering is not necessary. Therefore it is possible to make Ti_3AlC_2 or Ti_2AlC powders from

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cheap TiH_2 by a simple process, pressureless sintering, without preliminary dehydrogenation.

In literatures, it was reported that Sn[13] or Si[14,15] additives in starting materials promote the fabrication of Ti_3AlC_2 and reduce the content of impurity TiC. However, no literature reports are yet available on the synthesis of Ti_3AlC_2 from TiH_2 with Sn or Si as additive. In this paper, we incorporated the dehydrogenation and synthesis reactions in a single reactive pressureless sintering process to synthesize Ti_3AlC_2 or Ti_2AlC. Also the effect of Sn or Si as additive was considered.

2 Experimental

Starting powders of TiH_2 (325 mesh, 99 wt% pure, Jinzhou Haotian Titanium Co., China), Al (200 mesh, 99.99 wt% pure, Henan Yuanyang Aluminum Industry Co., China), TiC (200 mesh, 99.8 wt% pure, Aladdin Reagent Co., China), Sn (99.99 wt% pure, Tianjin Chemical Reagent Institute, China), Si (99 wt% pure, Tianjin Weimeng Chemical Reagent Co., China) were employed in this research. The powders to fabricate Ti_3AlC_2 were mixed in molar ratio of TiH_2 /2TiC/x Al (x=1, 1.1, 1.2). The starting materials of $3TiH_2/1.5Al/C$ and $2TiH_2/1.5Al/$ TiC were chosen to synthesis Ti_2AlC. These powders were mixed by an airport star mixing machine for 4 hr. Some powders were then compacted in a steel mould with the diameter of 12 mm to research the effect of cold-compacted. Cold-compacted samples or samples without cold-compaction were put into alumina crucibles coated with hexagonal boron nitride spray. The samples were sintered by a tube furnace in flowing argon atmosphere at 1 200-1 500 ℃ for 120 min. The heating rate was 10 ℃/min below 500 ℃, 20 ℃/min between 500 ℃ to 900 ℃, and 25 ℃/min above 900 ℃. The schematic sintering procedure is showed in Fig.1. The sintered compacts were pulverized and ground into powders, and X-ray diffraction (XRD, Brukeraxs Co., Germany) with Cu Kα radiation at 40 kV and 40 mA was applied to estimate phase compositions. Fracture surface of collected samples were examined by scanning electron microscopy (SEM, JSM-6390LV, JEOL, Japan) to reveal the microstructure.

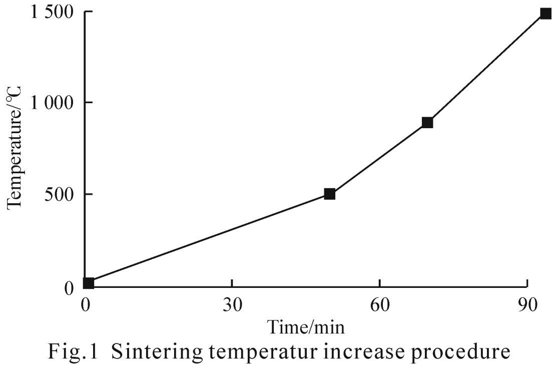


Fig.1 Sintering temperatur increase procedure

3 Results

3.1 XRD results

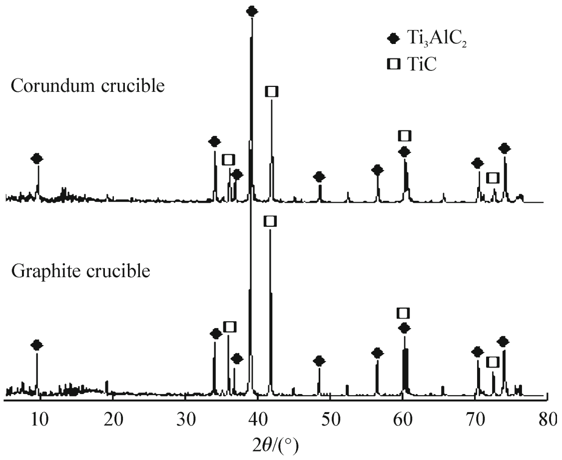
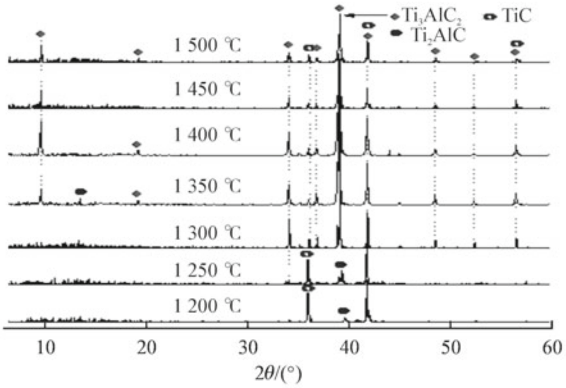


Fig.2 XRD patterns of $3TiH_2/Al/2C$ sintered at 1 400 ℃ for 120 min in different conditions

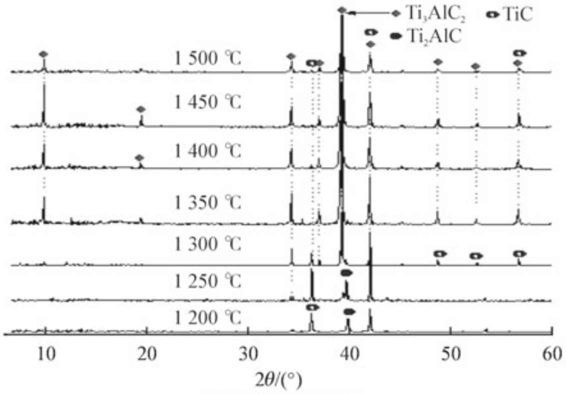
Two samples were synthesized from starting materials compacts in disc shape made by cold pressing. Others were synthesized from the directly mixture powders without compression. The synthesized samples from directly mixed powders and cold pressed powders have pretty similar XRD patterns if synthesizing time was the same. Directly mixed powders are simple and convenient in a commercial run, thus only XRD results of samples with directly mixed powders as raw materials were researched and are shown in this paper. Fig.2 shows XRD patterns of the samples sintered at 1 400 ℃ for 120 min in different containers (graphite crucibles and corundum crucibles).

Fig.3 shows the X-ray diffraction patterns of the mixed powders of TiH_2/x Al/ 2TiC (x=1, 1.1, 1.2) sintered at 1 200-1 500 ℃ for 120 min. After heat treat at 1 200-1 250 ℃ for 120 min, two phases were confirmed, *i e*,Ti_2AlC and TiC. Ti_3AlC_2 could not be fabricated at this temperature range. TiC was the dominating phase. If the sample was sintered at 1 300 ℃ for 120 min, Ti_3AlC_2 was the main synthesized phase. As sintering temperature increased, the relative intensity of Ti_2AlC peaks and TiC peaks decreased gradually. Even more, if the sintering temperature was at 1 300-1 500 ℃, almost single-phase Ti_3AlC_2 phases (from XRD pattern) was synthesized in 120 min.

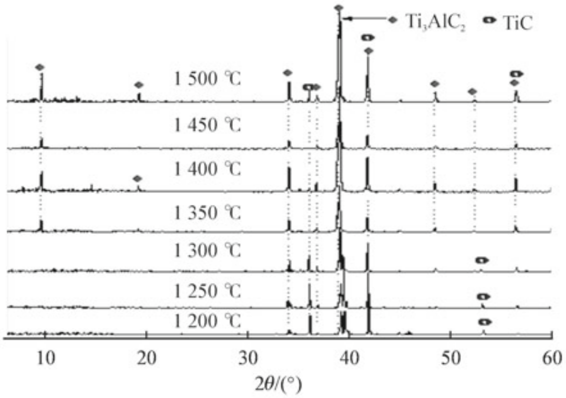
Even better results could be obtained if Si or Sn powders were used as additives as shown in Fig.4. Especially, the addition of Sn or Si powders decreases the sintering temperature to 1 200 ℃ and soaking time to 60 min.



(a) $TiH_2/Al/2TiC$



(b) $TiH_2/1.1Al/2TiC$



(c) $TiH_2/1.2Al/2TiC$

Fig.3 XRD patterns of (a) $TiH_2/Al/2TiC$, (b) $TiH_2/1.1Al/2TiC$ and (c) $TiH_2/1.2Al/2TiC$ sintered at different temperatures for 120 min

The proportions of the constituent phases of Ti_3AlC_2, Ti_2AlC and TiC in the synthesized products can be estimated from the integrated XRD peak intensities according to the following equations[17]:

$$W_a = \frac{I_a}{I_a + 0.16I_b + 0.10I_c} \quad (1)$$

$$W_b = \frac{I_b}{6.25I_a + I_b + 0.60I_c} \quad (2)$$

$$W_c = \frac{I_c}{10.0I_a + 1.67I_b + I_c} \quad (3)$$

where, W_a, W_b and W_c are the mass percentages of Ti_3AlC_2, Ti_2AlC and TiC, respectively. I_a, I_b and I_c are the integrated diffraction intensity of Ti_3AlC_2 (002), Ti_2AlC (002) and TiC (111) peaks, respectively.

Fig.5 shows Ti_3AlC_2 purity of samples sintered at different temperature for 120 min. From Fig.5, a conclusion could be drawn that the best result (95 wt% Ti_3AlC_2) is from $TiH_2/1.1Al/2TiC$ at 1 450 ℃. Nevertheless, Ti_3AlC_2 content decrease at 1 500℃ from raw materials of $TiH_2/1.1Al/$ 2TiC and $TiH_2/1.2Al/2TiC$.

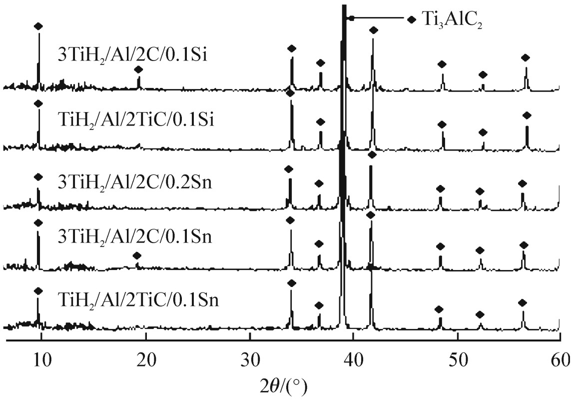


Fig.4 XRD patterns of $TiH_2/Al/2TiC/x$ Sn (Si) at 1 200 ℃ for 60 min

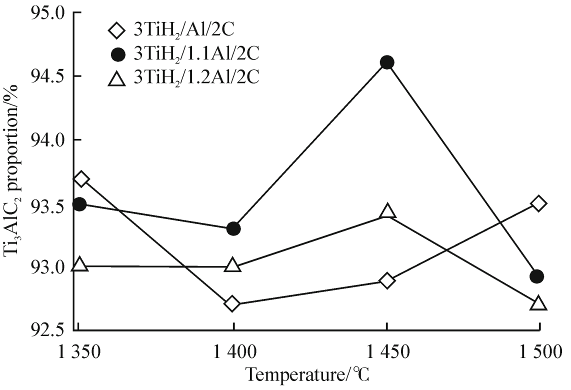


Fig.5 Relationship between sintering temperature and Ti_3AlC_2 proportion

3.2 Microstructure

Scanning electron microscope (SEM) observation was made on various samples. As an example, the results for the sample with $TiH_2/1.1Al/2TiC$ composition sintered at 1 400 ℃ and 1 500 °C are shown in Fig.6 and Fig.7, respectively. From Fig.6, the average grain diameter is about 3-5 μm (inset of Fig.6). The surface of most Ti_3AlC_2 grains was smooth and with obviously lamellar structure (Fig. 7).

Figs.8-9 show the SEM images of Ti_2AlC samples sintered at 1 300 ℃ for 120 min by similar methods. Fig.8 shows the overall morphology and Fig.9 is an image with high magnification. The size of most plate-like grains is about 3-6 μm in diameter and 1-2 μm in thickness.

The effect of additives (Si, Sn) on variation of grain size was also researched. The microstructures of samples from 3TiH$_2$/Al/2C/0.1Si or 3TiH$_2$/Al/2C/0.1Sn sintered 1 200 ℃ are shown in Figs.10-12. At low magnification, the whole structure is compact nearly without pores (Fig.10 and Fig.12) compared with the samples sintered without additives (Fig. 6 and Fig.8). The lamellar structure of Ti$_3$AlC$_2$ is shown in Fig.11.

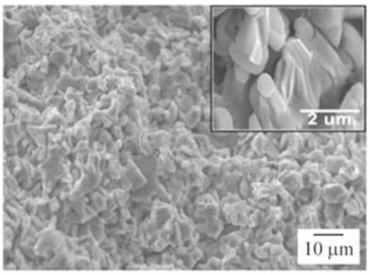


Fig.6 SEM images of sample sintered at 1 400 ℃ from TiH$_2$/1.1Al/2TiC

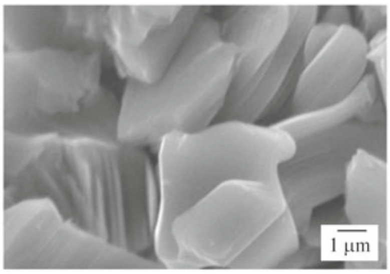


Fig.7 SEM image of sample sintered at 1 500 ℃ from TiH$_2$/1.1Al/2TiC

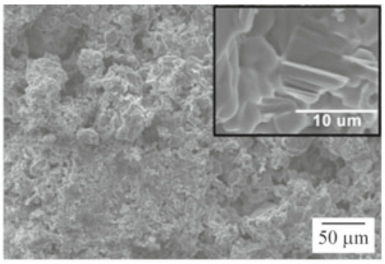


Fig.8 SEM images of Ti$_2$AlC sample sintered at 1 300 ℃ for 120 min

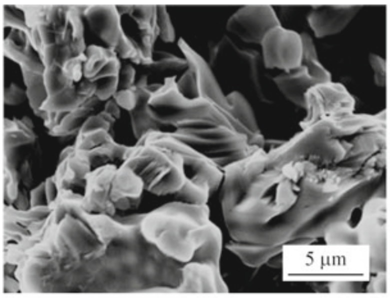


Fig.9 SEM image of plate-like grains in the sample of Ti$_2$AlC sintered at 1 300℃ for 120 min

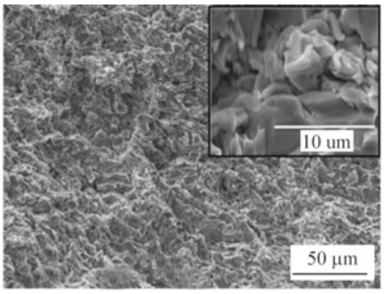


Fig.10 SEM images of sample sintered at 1 200 ℃ for 60 min from TiH$_2$/Al/2TiC/0.1Si

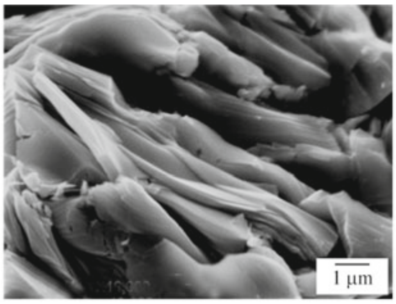


Fig.11 SEM image of Ti$_3$AlC$_2$ lamellar structure

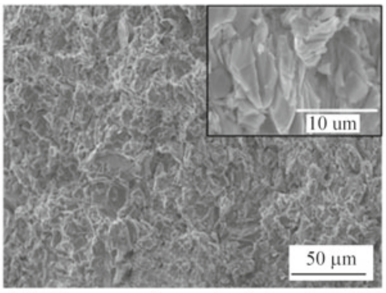


Fig.12 SEM images of sample sintered at 1 200 ℃ for 60 min from TiH$_2$/Al/2TiC/0.1Sn

From the figure, the lamellar structure of Ti$_3$AlC$_2$ is more identifiable and the grains are much larger and thinner. The usual grain size was 8-10 μm in diameter and about 1 μm in thickness (Fig.11). However, the microstructures of all the samples still contain some fine grains with no more than 1 μm in diameter.

3.3 Physical properties

Ti AlC$_2$ and Ti$_2$AlC both exhibited excellent ductility. A single phase Ti$_3$AlC$_2$ porous bulk in disc shape was pressed at room temperature by a universal testing machine (WEW-1000B, Jinan Shijin Group Co., LTD, China). The ductile deformation was amazing. The diameter of the Ti$_3$AlC$_2$ disc extended from 12 to 20 mm and the thickness decreased from 6 to 1 mm.

The densities of as-synthesized Ti$_3$AlC$_2$ was 2.9 -3 g/cm^3, which was rather low compared with the theoretical density, 4.25 g/cm^3. Therefore this method is just applied to produce powders or porous samples.

4 Discussion

4.1 Effects of containers and cold pressing

From Fig.2, graphite crucible is a disadvantage for the formation of Ti_3AlC_2 compared with corundum crucible. This is because carbon atoms from graphite crucible diffuse into the starting materials at high temperature and change the relative ratios of starting powders. Therefore it is difficult to fabricate high purity Ti_3AlC_2 in graphite crucible.

4.2 XRD of Ti_3AlC_2

Because the evaporation of Al at high temperature, three kinds of raw materials were sintered at 1 200-1 500 ℃ for 120 min. According to Fig.3, the as-synthesized samples had almost identical XRD patterns if synthesizing time was same. The dominating phases were Ti_2AlC and TiC at 1 300 °C, while high pure Ti_3AlC_2 was fabricated at 1 350 °C - 1 500 °C. It was concluded that the best sintering temperature was 1 350 °C for TiH_2/Al/2TiC (Fig.3(a)), 1 450 ℃ for TiH_2/ 1.1Al/2TiC (Fig.3(b)) and 1 450 ℃ for TiH_2/1.2Al/2TiC (Fig.3(c)). An important phenomenon was noted that higher sintering temperature (1 500 ℃) did not make contribution on the fabrication of single phase Ti_3AlC_2 (Fig.3(c)).

4.3 Purity of Ti_3AlC_2

According to previous research[2], Ti_3AlC_2 begins to decompose into TiC and Ti_2AlC at high temperature. Compared with the samples synthesized from TiH_2/1.1Al/2TiC, the samples from TiH_2/1.2Al/2TiC usually contain less Ti_3AlC_2, which suggests that superfluous Al powders are not favorable for the fabrication of single-phase Ti_3AlC_2.

4.4 Microstructure

From Fig. 6, the sample is porous and easy to be broken for making powders. The porous structures can be explained from two aspects. On one hand, the sintering process is under a pressureless condition. Although the material powders form liquid phase at high temperature, there is no assistant drive force to densify. On the other hand, the holes may be the trace of dehydrogenation of TiH_2.The dehydrogenation of TiH_2 is a lasting process during the whole sintering course rather than just at a certain temperature period[16].

The typical grain size had a trend to increase with the elevating of sintering temperature (inset of Fig.6 and Fig.7). This result agrees with the conclusions that high temperature accelerates the grain growth.

The samples in Fig.8 are much more porous than that in Fig.6. It is because more TiH_2 was used in starting material for samples in Fig.8. Thus if more TiH_2 is used in starting materials, the cost of Ti_3AlC_2 is cheaper and easier to be ground into powders.

From the comparison between the samples with additives of Sn and Si powders, the samples with Sn additives were much more compacted and regular in the same synthesis condition (Fig.10 and Fig.12). It can be attributed to Sn's lower melting point. Conversely, the melting point of Si is 1 412 ℃; it is difficult to form liquid phase during the sintering process.

4.5 Reaction mechanisms

For the sintering method at this paper, the dehydrogenation of TiH_2, besides temperature and time, is also an important factor affecting the fabrication of Ti_3AlC_2 and Ti_2AlC. To clearly understand the reaction mechanism from the point of view of thermodynamics, a differential scanning calorimeter (DSC, Setaram Evolution 2400) was used to reflect the heat changing during heat treatment. Fig.13 shows DSC curves of Ti/1.2Al/2TiC and TiH_2/1.2Al/2TiC heated by the procedure of Fig. 1 in Ar atmosphere. From this figure, the DSC curves appeared an obvious sharp endothermic peak at about 660 ℃, near the melting temperature of Al, for both raw materials. This peak is due to the melting of Al. A broad exothermic peak (900-1 100℃) appeared for the mixture of Ti/1.2Al/2TiC, which is due to the exothermic reaction among Ti, Al and TiC to form binary or ternary compound, such as Ti_3AlC_2[18]. However there is no obvious peak at this temperature range for the mixture of TiH_2/1.2Al/2TiC. It is because that the dehydrogenation of TiH_2 at this temperature range is endothermic and balance out the exothermic reaction to form new compounds. It is suggested that the thermal explosion, a major hassle to synthesis Ti_3AlC_2, can be avoided if TiH_2 powders replaces Ti powders as Ti source.

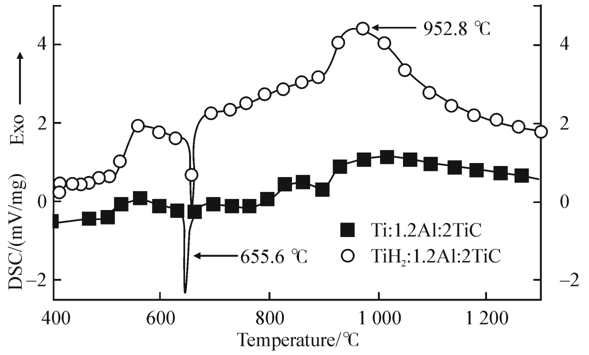


Fig.13 DSC curves of Ti/1.2Al/2TiC mixture and TiH_2/1.2Al /2TiC mixture in highly pure Ar

At previous research, some scholars[10, 11] deemed that C atoms in TiC diffused into the TiH_2, resulting the expansion of the TiH_2 lattice and increasing the overflow speed of H atoms from the TiH_2 structure. Nevertheless, Al atoms are easier to diffuse into the TiH_2 lattice compared with C atoms of TiC at high temperature, because Al powders transform to liquid phase at temperature above 660 ℃ (Fig.13), which provides the circumstance for chemical reactions. The liquid Al can prompt the dehydrogenation of TiH_2 and generate Ti atoms solved in Al melt. The chance of reaction between Ti and Al is much larger than that of the reaction between Ti atoms and C atoms.

Why the additive (Sn) can promote the formation of pure Ti_3AlC_2? It can be explained from two aspects. On one hand, the melting point (about 232 ℃) of Sn is lower than that of Al (about 660 ℃). Ti-Sn alloy can be formed at 600 °C. The Sn rich liquid phase accelerates the reactions among Ti, Al and C. On the other hand, Sn atoms can substitute some Al atoms in the crystal cells of Ti_3AlC_2 and Ti_2AlC, forming $Ti_3Al_{(1-x)}Sn_xC_2$ and $Ti_2Al_{(1-y)}Sn_yC$ ($x + y = 0.1$) solid solutions, respec-tively [2,17]. These solid solutions gear up the transformation from Ti_2AlC into Ti_3AlC_2. Hence, there is only Ti_3AlC_2 peaks (Fig.4).

5 Conclusions

a) Ti_3AlC_2 porous samples can be synthesized from cheap powders mixture of TiH_2/x Al/2TiC (x=1, 1.1, 1.2) by a simple method (PLS) at 1 300-1 500 ℃ for 120 min without preliminary dehydrogenation. 95 wt% pure Ti_3AlC_2 was synthesized from TiH_2/1.1Al/2TiC at 1 450 ℃. Overall morphology of the sample was porous and easy to be broken into powders.

b) Single-phase Ti_3AlC_2 was obtained at 1 200 ℃ for 60 min by the addition of Sn or Si in the starting materials with TiH_2 as Ti source. The microstructure was more compact and nearly without porous. Single phase Ti_3AlC_2 porous bulks had excellent ductility at room temperature.

c) If TiH_2 is used as Ti source to synthesis Ti_3AlC_2, thermal explosion due to exothermic reaction of the formation of Ti_3AlC_2 can be avoided. The diffusion of Al atoms to crystal lattice of TiH_2 promotes the dehydration of TiH_2.

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