Preparation of Ti_3AlC_2 by mechanically activated sintering of 3Ti/Al/2C/0.2Sn

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Abstract. The mechanically activated sintering process was adapted to synthesize titanium aluminum carbide (Ti_3AlC_2) at low temperature. A mechanically induced self-propagation reaction occurred by mechanical alloying of 3Ti/Al/2C powder mixtures. In addition to powder products, a large amount of rigor granules with a size of 0.5 ~ 10 mm were produced. Fine powders containing Ti_3AlC_2 , Ti_2AlC and TiC were obtained. The granules composed of Ti_3AlC_2 , Ti_2AlC and TiC. Adding Sn may remove Ti_2AlC and enhance the synthesis of Ti_3AlC_2 . After Sn was added, the products only contained Ti_3AlC_2 and TiC. The Ti_3AlC_2 content of the powders and granules were 75 wt% and 88 wt%, respectively. The mechanically alloyed products were pressureless sintered at 900–1300°C for 2 h. Sintering of these products at 900 ~ 1200°C yields samples containing over 95 wt% Ti_3AlC_2 . The sintered powder compacts with high purity Ti_3AlC_2 had a fine organization. The lath Ti_3AlC_2 of the granules had a length of 10–20 μm .

Keywords. Ti_3AlC_2 ; mechanically activated sintering; Sn.

1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) has received increasing attention because it shows both ceramic and metallic properties simultaneously (Tzenov and Barsoum 2000; Zou *et al* 2007). For example, it has low density, good electrical and thermal conductivity, high thermal shock, good oxidation resistance, good workability, etc.

Ti_3AlC_2 powders can be synthesized by combustion synthesis (Ge *et al* 2003; Chen *et al* 2004), heat treatment (Ai *et al* 2006; Peng *et al* 2006), pressureless sintering (Peng *et al* 2004). Though combustion synthesis has the potential of time saving, low energy requirement, the highest content of the obtained Ti_3AlC_2 materials was less than 90 wt% (Ge *et al* 2003; Chen *et al* 2004). Ti_3AlC_2 powders with high purity were obtained by heat treatment and pressureless sintering (Ai *et al* 2006; Peng C 2004; Peng C Q *et al* 2006). However, these methods usually require higher temperature (> 1300°).

Mechanical alloying is a convenient process of synthesis that has low fabrication cost and high amount yields. Ti_3AlC_2 materials have been synthesized by MA 3Ti/Al/2C powder mixtures (Li *et al* 2006; Yang *et al* 2009). However, it is difficult to synthesize Ti_3AlC_2 with high purity by single MA process. Recently, Li *et al* (2007) synthesized Ti_3AlC_2 by mechanically activated sintering 3Ti/Al/2C powders. However, high content of Ti_3AlC_2 was

obtained at 1350°C. The sintering temperature for synthesizing Ti_3AlC_2 is still relatively higher.

The literature (Ai *et al* 2006) pointed out that the addition of Sn effectively inhibited the generation of thermal explosion and also inhibited the forming of TiC and other impurities, and considerably reduced the lower limit synthesis temperature. Additionally, $\text{Ti}_3(\text{Al}, \text{Sn})\text{C}_2$ solution materials were fabricated by different sintering processes (Ai *et al* 2007; Manoun *et al* 2007).

In this study, Ti_3AlC_2 with high purity was synthesized by mechanically activated sintering process using 3Ti/Al/2C/0.2Sn as the raw materials at low temperature.

2. Experimental

Ti powder (99.6% pure, 50 μm), Al powder (99.0% pure, 20 μm), Sn powder (99.0% pure, 50 μm) and graphite powder (99.0% pure, 50 μm) were mixed in a mole ratio calculated from 3Ti/Al/2C/0.2Sn. MA was carried out in a planetary ball mill (XM-4x05) with stainless-steel milling containers and bearing steel ball. The rotation speed was set as 250 rpm. The mass ratio of the ball to the powder was 20 : 1. The powders were taken out at 6 h. The MA powders were formed as billets by die pressing at 50 MPa. The compacts were sintered at a temperature of 900–1300°C for 2 h in vacuum (~20 Pa). The heating rate was 15°C/min. XRD analysis was carried out using a rotating anode X-ray diffractometer (Model D/MAX-2500PC) with $\text{CuK}\alpha$ radiation. Scanning electron micro-

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scopy (SEM) was carried out with a KYKY-2800 apparatus equipped with energy-dispersive spectroscopy (EDS). Based on the XRD profiles, the weight fraction of Ti_3AlC_2 fabricated in the as-synthesized product was calculated based on the following equation (Xu *et al* 2006):

$$W_{\text{TiC}} = \frac{1.084}{(I_{A(104)} / I_{T(111)} + 1.084)} W_{\text{TAC}} = 1 - W_{\text{TiC}}, \quad (1)$$

where W_{TiC} is the weight fraction of TiC, W_{TAC} the weight fraction of Ti_3AlC_2 and $I_{A(104)} / I_{T(111)}$ the integrated diffraction intensity ratio of TiC to Ti_3AlC_2 main peaks obtained from the XRD patterns. Density was determined using the Archimedes method. The relative density was

calculated according to the Ti_3AlC_2 content and the theoretical densities of Ti_3AlC_2 and TiC, being 4.25 and 4.90, respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of the mechanically alloyed products synthesized by MA using 3Ti/Al/2C/XAl (X = 0, 0.20) mixed powders as raw material. After reacting, amounts of rigor granules with a size of 0.5–10 mm were obtained (as shown in figure 2). This is an important factor that Ti_3AlC_2 is synthesized by mechanically induced self-propagation reaction. As illustrated in figure 1, when the raw material was a 3Ti/Al/2C powder mixture, the powder products composed of TiC, Ti_3AlC_2 and Ti_2AlC . And the strong peaks of Ti_3AlC_2 and Ti_2AlC had weaker intensity than those of TiC. When Sn was added, the relative peak intensity of Ti_3AlC_2 peaks of the powders was higher than that of TiC, and Ti_2AlC peaks absent. The XRD result indicates that adding Sn removed Ti_2AlC and enhanced the synthesis of Ti_3AlC_2 obviously.

No matter whether Sn was added, the granules composed of Ti_3AlC_2 and TiC. The strongest peaks of Ti_3AlC_2 were always somewhat stronger than those of TiC, suggesting that Ti_3AlC_2 content of the granules was much higher than that of the powders.

Figure 1. XRD patterns of products obtained by MA of (a) 3Ti/Al/2C and (b) 3Ti/Al/2C/0.20Sn.

Figure 2. Appearance of the granules.

The XRD results showed that appropriate Sn could enhance the synthesis of Ti_3AlC_2 of the powders significantly.

Figure 3 shows the morphology of the mechanically alloyed products obtained by MA of $3\text{Ti}/\text{Al}/2\text{C}/0.2\text{Sn}$. The milled powders were fine with a size of $0.5 \sim 7 \mu\text{m}$. In fact, these big particles were composed of some fine particles. The granules composed of lots of TiC around grains with a size of about $2 \mu\text{m}$ and Ti_3SiC_2 platelets with a size of $\sim 10 \mu\text{m}$ (identified by EDS).

Figure 4 shows XRD of the mechanically alloyed product sintered at different temperatures. These sintered samples consisted of Ti_3AlC_2 and TiC. At temperature of $900\text{--}1200^\circ\text{C}$, the intensity of Ti_3SiC_2 main peaks of the mechanically alloyed products was much higher than those of TiC. TiC peaks were quite weak, indicating its content was very low. However, when the temperature was 1300°C , the relative intensity of Ti_3AlC_2 peaks of both products obviously decreased, which was almost equal to those of TiC.

Figure 3. (a) Morphology of the powders and (b) fracture morphology of the granule.

Figure 5 shows schematic of Ti_3AlC_2 content in the sintered samples. At $1000\text{--}1200^\circ\text{C}$, the content of Ti_3AlC_2

Figure 4. XRD patterns of (a) powders and (b) granules obtained by mechanically activated sintering of $3\text{Ti}/\text{Al}/2\text{C}/0.2\text{Sn}$.

Figure 5. Schematic of the Ti_3AlC_2 content in the sintered samples.

Figure 6. Fracture morphology of the powder compacts with high purity Ti_3AlC_2 sintered at (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C and (e) 1300°C.

in the samples was over 95wt%. However, the content of Ti_3AlC_2 in the powder and granule samples decreased to 50 wt% and 65 wt%, respectively.

Figure 6 shows fracture morphology of the sintered powder compacts at different temperatures. At 900°C, it composed of many fine grains with a size of 1–2 μm . With an increase of temperature from 1000–1300°C, the grains gradually grew up and finally developed to lath

grains with a size of 10 μm . Additionally, the organization of the compacts became more and more denser with increasing temperature. At 1200–1300°C, the relative density reached 97% and 98.1%, respectively. Obviously, the fine milled powder particles (as was shown in figure 3) facilitate to the sintering densification of the compact.

Figure 7 shows SEM of Ti_3AlC_2 granules sintered at 900–1200°C. All organization of the granules were similar.

Figure 7. Fracture morphology of the granules with high purity Ti_3AlC_2 sintered at (a) 900°C, (b) 1000°C, (c) 1100°C and (d) 1200°C.

These samples consisted of Ti_3AlC_2 flake crystalline grains with a length of 10–20 μm and small amounts of TiC around grains with a size of 2 μm .

From above results, after sintering at 900–1200°C, the samples with high purity, Ti_3AlC_2 , were obtained. However, Ti_3AlC_2 partially decomposed to TiC at 1300°C.

In this study, Ti_3AlC_2 with high purity could be fabricated by mechanically activated sintering at 900–1200°C. The temperature of the fabrication of high purity Ti_3AlC_2 decreased by 400°C compared with literatures (Peng C *et al* 2004; Ai *et al* 2006; Peng C Q *et al* 2006).

The main reason for enhancing the synthesis of Ti_3AlC_2 at low temperature can be to contribute to the effect of Sn on the synthesis of Ti_3AlC_2 via MA and subsequent sintering. On adding Sn into the raw materials, it can promote the synthesis of $\text{Ti}_3\text{Al}(\text{Sn})\text{C}_2$ (Ai *et al* 2006, 2007; Manoun 2007). Additionally, the literature (Li *et al* 2008) pointed out that addition of appropriate Sn promoted the transformation of Ti_2AlC into Ti_3AlC_2 . It contributed to the dissolution of Sn into the crystal structure of Ti_2AlC , leading to an unstable structure reducing the conversion energy of Ti_2AlC to Ti_3AlC_2 . Therefore, adding of Sn enhanced the synthesis of $\text{Ti}_3\text{Al}(\text{Sn})\text{C}_2$ and improved the phase purity of Ti_3AlC_2 in the products.

4. Conclusions

Adding Sn may enhance the synthesis of Ti_3AlC_2 obviously by mechanically activated sintering. With a temperature of 900–1200°C, the sintered samples containing over 95 wt% Ti_3AlC_2 were obtained.

References

- Ai M X, Zhai H X, Zhou Y, Tang Z Y, Huang Z Y, Zhang Z L and Li S B 2006 *J. Am. Ceram. Soc.* **89** 1114
- Ai M X, Zhai H X, Liang S G and Liang Z Y 2007 *Rare Metal. Mater. Eng.* **36** 150
- Chen K, Guo J, Ning X, Zhou H, Fu R and Ferreira J M F 2004 *J. Ceram. Soc. Jap.* **11** 2428
- Ge Z, Chen K, Guo J, Zhou H and Ferreira J M F 2003 *J. Euro. Ceram. Soc.* **23** 567
- Li S B, Zhai H X, Bei G P, Zhou Y and Zhang Z L 2006 *Mater. Sci. Technol.* **22** 667
- Li S B, Zhai H X, Bei G P, Zhou Y and Zhang Z L 2007 *Ceram. Int.* **33** 169
- Li S B, Xiang W H, Zhai H X, Zhou Y and Li C W 2008 *Mater. Res. Bull.* **43** 2092
- Manoun B, Saxena S K, Hug G, Ganguly A, Hoffman E N and Barsoum M W 2007 *J. Appl. Phys.* **101** 1

- Peng C, Wang C, Qi L and Huang Y 2004 *Mater. Sci. Forum* **475** 1247
- Peng C Q, Wang C A, Song Y and Huang Y 2006 *Mater. Sci. Eng.* **A428** 54
- Tzenov N V and Barsoum M W 2000 *J. Am. Ceram. Soc.* **83** 825
- Xu Xue-wen, Fu Cheng-ke, Li Yang-xian, Zhu Jiao-qun and Mei Bing-chu 2006 *Trans. Nonferrous Met. Soc. China* **16** 490
- Yang C, Jin S Z, Liang B Y, Liu G J and Jia S S 2009 *J. All Compd.* **209** 871
- Zou Yong, Sun Zheng Ming, Hashimoto Hitoshi and Tada Shuji 2007 *Mater. Trans.* **48** 2432