

An X-ray diffraction study of the texture of Ti_3SiC_2 fabricated by hot pressing

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Abstract

Bulk sample of Ti_3SiC_2 was synthesized by hot pressing from Ti, SiC and graphite powders with 20 vol.% TiC as the second phase. Two samples were prepared to perform XRD experiments: one was the bulk sample whose faces paralleled to the pressing surface, and the other was powder, which was milled from the former bulk sample. These two XRD patterns were further corrected to get more precise data. The results indicated that in bulk sample Ti_3SiC_2 phase possessed strong texture, whereas TiC phase did not possess texture. The relative orientation density, J_{hkl} , was calculated for each crystal plane of Ti_3SiC_2 phase. The results also showed that the basal plane in Ti_3SiC_2 phase preferred not to parallel to the pressing surface. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ti_3SiC_2 is a remarkable material for it possesses a combination of unique properties. Its electrical and thermal conductivities are higher than those of pure Ti metal. The Ti_3SiC_2 material has good oxidation resistance and is also not susceptible to thermal shock.¹ There are many ways to synthesize the bulk Ti_3SiC_2 material, such as HIP, SHS, HP etc. Among these ways, hot pressing with Ti, SiC and graphite powders is an economic and convenient method. Due to the different synthesis methods and the different machining procedures, the bulk samples have different XRD data (especially the strongest intensity peak). For example: in Goto and Hirai's work² where Ti_3SiC_2 was fabricated by chemical vapor deposition (CVD), the strongest intensity peak was the {008} peak in their powder XRD data. Yet in the work of Arunajatesan and Carrin,³ the strongest intensity peak was the {104} peak. Jiangtao and Miyameto⁴ used two different ways to fabricate Ti_3SiC_2 , the strongest intensity peaks were the peaks of {104} and {008} respectively. The divergence in XRD

data, which was mainly due to the influence of texture, resulted in some difficulties of purity calculation, phase determination and anisotropy analysis in Ti_3SiC_2 material. So the characteristics of texture are very important in investigating the Ti_3SiC_2 bulk material.

In this work, powder and bulk of Ti_3SiC_2 samples were used respectively to perform XRD experiment. Some useful information about the texture in bulk Ti_3SiC_2 sample were presented and analyzed.

2. Experimental procedure

The Ti, SiC and C powders were mixed with a stoichiometric molar ratio of 3:1:1 and cold pressed at 80 MPa pressure. The green body was put into graphite die with BN to prevent the sample from sticking to the die walls. The sample was sintered in flowing argon gas, at 1600°C under 25 MPa pressure for 5 h. After polishing, the face paralleled to the pressing surface (perpendicular to the press direction) was examined by XRD ($\text{CuK}\alpha$ diffraction). After that, a powder XRD sample was made by milling the former bulk sample with the particle size less than 20 μm . In order to get more precise data, the background scattering was eliminated and

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$K_{\alpha,1}$, $K_{\alpha,2}$ diffraction was separated. The face parallel to the pressing surface of the bulk sample was observed by scanning electron microscopy (SEM).

3. Result and discussion

Figs. 1 and 2 are XRD patterns of the powder and bulk samples, respectively. From Fig. 1 and 2, mainly two phases (Ti_3SiC_2 , and TiC) are found in the samples, and other phases almost do not exist. XRD data of Ti_3SiC_2 and TiC phases for Fig. 1 are listed in Tables 1 and 2 respectively, and those for Fig. 2 are listed in Table 3 and 4 respectively. From Table 1, the powder XRD data of Ti_3SiC_2 are very similar to those in Goto and Hirai's work,² especially the I/I_0 of the 3 strongest peaks. Because Goto and Hirai fabricated the sample by the CVD method,² which is different from our HP method, the data in their work are worth trusting as a standard in purity analysis and phase determination of Ti_3SiC_2 material. Since the bulk sample might possess texture, the powder XRD data are used to calculate the percentage of Ti_3SiC_2 phase in our sample. The ratio of theoretical intensity for the $\{002\}$ plane in TiC phase to

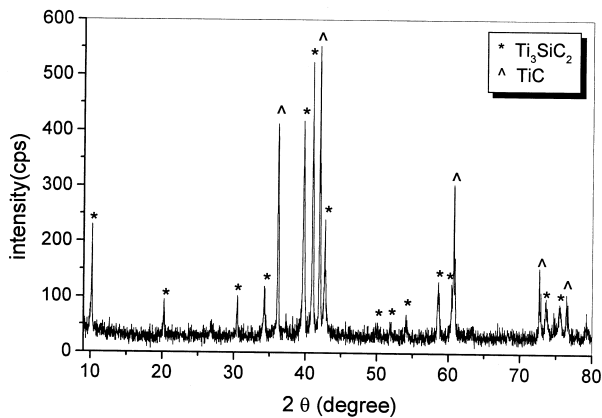


Fig. 1. XRD Pattern of powder sample.

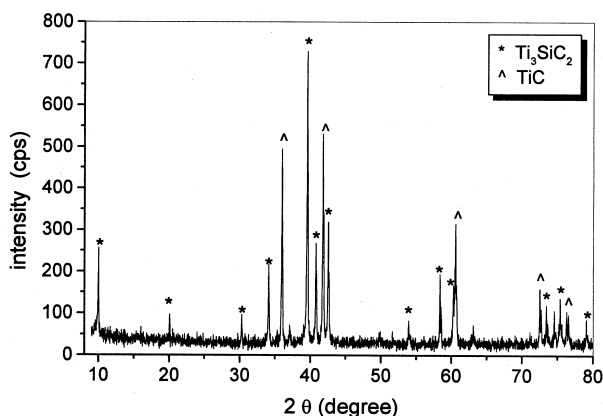


Fig. 2. XRD Pattern of bulk sample.

Table 1
The XRD data of Ti_3SiC_2 phase in mixed powder sample

| hkl | d (Å) | I_{hkl}^0 (cps) | 2θ (degree) | I/I_0 (%) | I/I_0 in work ² (%) |
|------|---------|--------------------------|--------------------|-------------|----------------------------------|
| 002 | 8.699 | 98 | 10.16 | 26 | 22 |
| 004 | 4.383 | 48 | 20.24 | 13 | 11 |
| 006 | 2.928 | 56 | 30.50 | 15 | 13 |
| 101 | 2.616 | 64 | 34.24 | 17 | 16 |
| 104 | 2.268 | 276 | 39.70 | 74 | 75 |
| 008 | 2.201 | 375 | 40.96 | 100 | 100 |
| 105 | 2.115 | 139 | 42.7 | 37 | 37 |
| 107 | 1.819 | 25 | 50.10 | 7 | 2 |
| 0010 | 1.762 | 26 | 51.84 | 7 | 3 |
| 108 | 1.695 | 30 | 54.04 | 8 | 5 |
| 109 | 1.575 | 79 | 58.54 | 21 | 19 |
| 110 | 1.529 | 69 | 60.48 | 18 | 13 |
| 1012 | 1.469 | 55 | 73.62 | 15 | 1 |
| 0014 | 1.258 | 49 | 75.5 | 13 | 13 |
| 205 | 1.241 | 23 | 76.68 | 6 | 3 |

Table 2
The XRD data of TiC phase in mixed powder sample

| hkl | d (Å) | I_{hkl} (cps) | 2θ (degree) | I/I_0 (%) | I/I_0 in JCPDS card (%) |
|-----|---------|------------------------|--------------------|-------------|---------------------------|
| 111 | 2.483 | 324 | 36.14 | 75 | 78 |
| 200 | 2.152 | 430 | 41.94 | 100 | 100 |
| 220 | 1.523 | 242 | 60.74 | 56 | 60 |
| 311 | 1.299 | 102 | 72.68 | 24 | 30 |
| 222 | 1.244 | 60 | 76.48 | 14 | 17 |

Table 3
The Ti_3SiC_2 XRD data for the face paralleled to the pressing surface in bulk sample

| hkl | d (Å) | I_{hkl} (cps) | 2θ (degree) | $J_{\text{hkl}}(I_{\text{hkl}}/I_{\text{hkl}}^0)$ | Angle to basal plane (degree) |
|------|---------|------------------------|--------------------|---|-------------------------------|
| 002 | 8.838 | 115 | 10.00 | 1.17 | 0 |
| 004 | 4.418 | 47 | 20.08 | 1.00 | 0 |
| 006 | 2.949 | 48 | 30.28 | 0.86 | 0 |
| 101 | 2.627 | 133 | 34.10 | 2.08 | 81 |
| 104 | 2.277 | 582 | 39.54 | 2.11 | 59 |
| 008 | 2.21 | 208 | 40.78 | 0.55 | 0 |
| 105 | 2.123 | 258 | 42.54 | 1.86 | 53 |
| 108 | 1.697 | 40 | 53.96 | 1.33 | 40 |
| 109 | 1.579 | 156 | 58.38 | 1.97 | 36 |
| 110 | 1.533 | 132 | 60.32 | 1.91 | 90 |
| 1012 | 1.288 | 78 | 73.46 | 1.42 | 29 |

Table 4
The TiC XRD data for the face paralleled to the pressing surface in bulk sample

| hkl | d (Å) | I_{hkl} (cps) | 2θ (degree) | I/I_0 (%) | I/I_0 in JCPDS card (%) |
|-----|---------|------------------------|--------------------|-------------|---------------------------|
| 111 | 2.494 | 363 | 35.98 | 83 | 78 |
| 200 | 2.160 | 435 | 41.78 | 100 | 100 |
| 220 | 1.526 | 252 | 60.60 | 58 | 60 |
| 311 | 1.302 | 135 | 72.52 | 31 | 30 |
| 222 | 1.247 | 67 | 76.30 | 15 | 17 |

that for the {008} plane in Ti_3SiC_2 phase is about 6:1, given the same incident beam cross-sectional area of these two planes. From the discussion above and Tables 1 and 2, the volume percentage of Ti_3SiC_2 phase in our samples is about 80%.

Since the heater and die of sintering furnace are made from graphite and the sintering time is long, the reaction below might take place in the last period of hot pressing.⁵

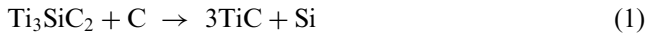


Fig. 3 shows the morphology of the face parallel to the pressing surface by SEM. The big grains are Ti_3SiC_2 , and the small bright ones are TiC, which disperse in the grain boundary or inside Ti_3SiC_2 grains.

According to Figs. 1 and 2, the most and the second strongest peaks of Ti_3SiC_2 are apparently different, which indicates that there may be texture in the bulk sample. By comparing Tables 2 and 4, the I/I_0 of the 3 strongest peaks of TiC in bulk and powder samples are both close to the data in JCPDS card. This indicates that in bulk sample TiC phase do not possess texture. There might be two reasons for this case: (1) according to the principle of maximum entropy, the TiC grains prefer to scatter disorderly and the crystal planes incline to orient randomly; (2) since the volume percentage of TiC phase is much less than that of Ti_3SiC_2 in the samples, during the sintering procedure of hot pressing, the growth of TiC grains are mainly restrained randomly by major Ti_3SiC_2 grains. Yet the macroscopic pressure, which mostly acts on the major phase Ti_3SiC_2 , has little influence on the growth of TiC grains.

As we know, the intensity of each {hkl} peak in Ti_3SiC_2 and TiC phase, I_{hkl} , is given as:⁶

$$I_{\text{hkl}} = \left(\frac{I_0 A_{\text{hkl}} \lambda^3}{32\pi r} \right) \left[\left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \frac{1}{v^2} \times \left[F^2 P \left(\frac{1 + \cos^2\theta}{\sin^2\theta \cos\theta} \right) \right] \frac{e^{-2M}}{2u} \quad (2)$$

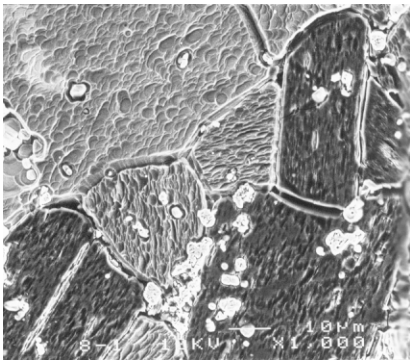


Fig. 3. Morphology of the face parallel to the pressing surface by SEM.

where, I_0 is the incident beam intensity, A_{hkl} is the incident beam cross-sectional area, λ is the incident beam wavelength, r is the radius of the diffractometer circle, μ_0 is a constant with a value of $4\pi \times 10^{-7} \text{ mkgc}^{-2}$, e is the electron charge, m is the electron mass, v is the unit-cell volume, F is the structure factor, P is the multiplicity factor, and u is the linear absorption coefficient for the mixture.

Because of the same ingredient in two samples, Eq. (2) could be written as:

$$I_{\text{hkl}} = K_{\text{hkl}} \cdot A_{\text{hkl}} \quad (3)$$

K_{hkl} has the same value for the same peak of the powder and bulk samples. Therefore, if I_{hkl} has the same value in both bulk and powder samples, the A_{hkl} has the same value, and vice versus. According to the above analysis, each crystal plane of TiC phase orients randomly in bulk and powder samples, thus A_{200} ({200} peak is the strongest peak in TiC phase) has a positive proportion to the total incident beam cross-sectional area (A_{total}) in both bulk and powder samples.

In order to calculate the degree of texture in bulk material, the relative orientation density, J_{hkl} , is presented as:⁷

$$J_{\text{hkl}} = \frac{A_{\text{hkl}}/A_{\text{total}}}{A_{\text{hkl}}^0/A_{\text{total}}^0} \quad (4)$$

where, A_{hkl} and A_{total} are respectively the incident beam cross-sectional area of {hkl} plane and total incident beam cross-sectional area in the bulk sample and A_{hkl}^0 and A_{total}^0 are respectively in the powder sample. I_{hkl} and I_{hkl}^0 are defined as the intensity of {hkl} peak of Ti_3SiC_2 phase in bulk sample and powder sample respectively.

From the discussion above, if I_{200} of TiC phase in powder sample is as same as that in bulk sample, so do A_{total}^0 and A_{total} in both samples. It is a coincident that I_{200} of TiC phase in powder XRD data (430 cps) is almost the same as that in bulk XRD data (435 cps), so A_{total} and A_{total}^0 can be considered as the same value. And in other cases, even if I_{200} of TiC phase in powder sample and that in bulk sample are not identical, we can multiply a certain coefficient to I_{hkl} of each crystal plane to make I_{200} same in both powder and bulk samples.

From Eq. (4), J_{hkl} can be expressed as:

$$J_{\text{hkl}} = \frac{A_{\text{hkl}}/A_{\text{total}}}{A_{\text{hkl}}^0/A_{\text{total}}^0} = \frac{A_{\text{hkl}}}{A_{\text{hkl}}^0} = \frac{I_{\text{hkl}}/K_{\text{hkl}}}{I_{\text{hkl}}^0/K_{\text{hkl}}} = \frac{I_{\text{hkl}}}{I_{\text{hkl}}^0} \quad (5)$$

The value of J_{hkl} can reflect the texture degree in bulk material of different crystal planes. When $J_{\text{hkl}} > 1$, {hkl} planes prefer to parallel to sample surface; when $J_{\text{hkl}} = 1$, {hkl} planes distribute randomly; and when $J_{\text{hkl}} < 1$, {hkl} planes do not prefer orientation parallel to the sample surface.

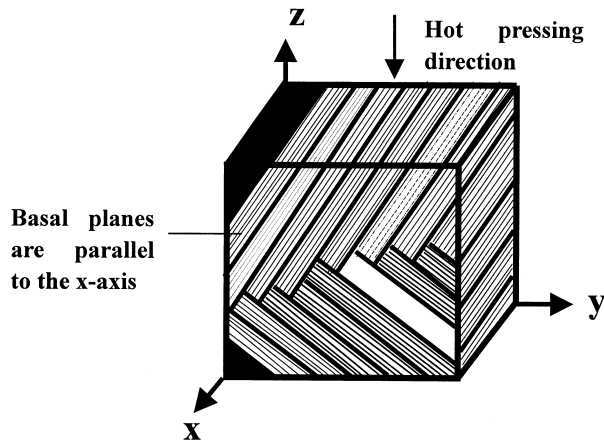


Fig. 4. Final grain orientation in Barsoum and El-Raghy's work.⁸

Table 3 shows the J_{hkl} value for each crystal plane of Ti_3SiC_2 phase in bulk sample. According to the J_{hkl} value and crystal plane indexes $\{hkl\}$, the planes can be divided into 3 groups:

For $\{10n\}$, J_{hkl} is bigger than 1, there are $\{101\}$, $\{104\}$, $\{105\}$, $\{108\}$, $\{109\}$, $\{1012\}$ planes, these six planes exhibit texture apparently.

For $\{00n\}$, J_{hkl} is less than or close to 1, there are $\{002\}$, $\{004\}$, $\{006\}$, $\{008\}$ planes, which have the same crystal orientation. Since the intensity of $\{002\}$, $\{004\}$, $\{006\}$ peaks are too weak to counteract errors in sample preparing and X-ray diffractometer, the data of $\{008\}$ plane can represent the characteristics of texture of $\{00n\}$ planes. Since $J_{008} = 0.55$, the $\{00n\}$ plane prefer not to parallel to the pressing surface.

For $\{110\}$, J_{hkl} is bigger than 1, because the $\{110\}$ planes are perpendicular to $\{00n\}$ planes, it is not difficult to consider that the $\{110\}$ planes had strong texture.

In Barsoum and El-Raghy's work,⁸ the bulk sample was further heated to 1600°C under load of 42 MPa and held at that temperature for 24 h. The relationship between the hot pressing direction and grain orientation (shown in Fig. 4) indicate that the basal plane inclines not to parallel to the pressing surface but slope to the pressing surface, this case is consistent with the results in our work.

4. Conclusion

1. In powder XRD analysis, the data in Goto and Hirai's work² is worth trusting as a standard in purity calculation and phase determination of Ti_3SiC_2 .
2. The TiC phase in bulk sample does not possess texture during the hot pressing procedure.
3. In the bulk sample, Ti_3SiC_2 possesses such a texture as $\{10n\}\langle uvw \rangle$, $\{110\}\langle uvw \rangle$. Many XRD data, where the strongest peak is $\{104\}$ peak ($2\theta = 39.7$), may be caused by the existence of texture.
4. In hot pressing, the basal plane in the Ti_3SiC_2 phase prefers not to be parallel to the pressing surface.

Acknowledgements

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