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Formation of TiC hexagonal platelets and their growth mechanism

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Abstract

A large amount of TiC hexagonal platelets has formed on the surface of the sample made of Ti/Si/TiC/$Al_{0.2}$ after sintering at above 1450 °C in an Ar atmosphere. The basal plane of TiC platelets is (111) facet confirmed by X-ray diffraction. Small amounts of Si and Al elements dissolved in the TiC crystal structure, influencing the structure of TiC. The detailed structure and growth mechanism of the TiC platelets have been observed and analyzed. A model has been proposed to understand the formation of TiC hexagonal platelets.
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Keywords: Hexagonal platelets; TiC; Microstructure; Growth mechanism

1. Introduction

Titanium carbide, TiC, has attracted much attention because of its high melting point, high modulus, great hardness, high chemical stability, *etc*. Hence it is an attractive compound for use as a high temperature ceramic and a reinforcing phase in composites.

TiC is a typical faceted crystal with a NaCl-type structure. It has been suggested that the growth unit of TiC is a TiC_6 octahedron. If the TiC_6 octahedra freely grew in liquid under equilibrium solidification, an ideal morphology of TiC particles with octahedral shape would be formed [1]. However, different growth kinetics, conditions and mechanisms can affect the growth morphology. For example, TiC particles with dendritic [1], rod [2], whisker or fiber [3–5], and hollow sphere shapes [6], *etc*. have been reported. The TiC rods, whiskers and fibers have been synthesized by the chemical vapor deposition (CVD) method through the vapor–liquid–solid (VLS) mechanism. However, TiC particles with dendritic, round and equiaxial shapes can in situ form in the Ti–Al–C or other systems by the solution-precipitation mechanism [1,7–10]. The relationship between the growth mechanisms and the morphologies of TiC has been extensively studied. Till now, no report on the formation of TiC hexagonal platelets is available.

Recently, a large amount of TiC particles with a hexagonal platelet shape has been first found during synthesis of Ti_3SiC_2 and Ti_3AlC_2 ternary compounds from Ti–Al–C and Ti–Si–C systems. In the present study, the main purpose is to observe the morphology of TiC and discuss its growth mechanism.

2. Experimental procedures

Ti (average particle size: 48 μm, >99% purity), Al (average particle size: 70 μm, >99.5% purity), TiC (average particle size: 4 μm, >99% purity) and Si (average particle size: 45 μm, >99% purity) powders were used in the present study.

The powders of Ti, Si, TiC and Al with a mole ratio of Ti:Si:TiC:Al=1:1:1:0.2 (denoted as Ti/Si/TiC/$Al_{0.2}$) and the powders of Ti, Si and Al with a mole ratio of Ti:Si:Al=1:1:0.2 (denoted as Ti/Si/$Al_{0.2}$) respectively were mixed. The mixed powders were cold pressed under 20 MPa to form compacts with a diameter of about 20 mm and a height of about 5 mm. The compacts were put into a graphite crucible and then pressurelessly sintered at different temperatures for 10 min in an argon atmosphere with a heating rate of 30 °C/min. The sintered samples were then characterized by X-ray diffraction (XRD) using a D/Max 2200PC diffractometer at 40 kV and 40 mA with Cu Kα radiation and scanning electron microscopy (SEM,

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model: STEREOSCAN 360) equipped with energy-dispersive spectroscopy (EDS).

3. Results and discussion

3.1. SEM observation and XRD identification of TiC platelets

Fig. 1 shows the SEM morphologies taken from the surface of the sintered samples. A large amount of TiC platelets forms with ~30 μm in size. Many TiC platelets possess a well-developed hexagonal characteristic (Fig. 1 (a)). A close observation shows that most of the platelets are composed of multiple thin platelets, and are thus called thick TiC platelets. The thin platelets stack together with a top–bottom sequence (Fig. 1 (b)). Each thin platelet is less than 1 μm in thickness. The upper thin platelet is smaller than the lower one, stacking and forming a stair feature (Fig. 1 (b)). However, other thin platelets with the same dimension and shape stack together perfectively, forming a thick platelet with a well-developed hexagonal shape (Fig. 1 (c)). All of the TiC platelets have a smooth surface, indicating that they precipitate from a liquid.

After sintering at 1500 °C, the sample surfaces are densely covered by TiC platelets (Fig. 2(a)). The platelets have stripes and are less than 30 μm in size. A clear observation from Fig. 2 (b) shows that these platelets are also thick platelets and composed of the thin platelets, similar to those shown in Fig. 1. Fig. 2 (c) shows the detailed structure of the TiC thick platelets, in which each TiC thin platelet is less than 0.5 μm in thickness. The thin platelets seem to be strongly bonded and form a brickwork structure.

An EDS spectra (Fig. 2 (d)) show that the platelets are mainly consist of Ti and C elements, small amounts of Al and Si element are also detected. This result proves that these platelets are TiC, and the Al and Si elements may dissolve into the TiC structure. It has been proved that Al or Si element can dissolve into the TiC structure and reduce its twin boundary energy [11].

Fig. 3 shows the XRD patterns of different phases. Fig. 3 (a) and (b) are the standard diffraction peaks for Ti_3SiC_2 (JCPDS card No.74-0310) and TiC (JCPDS card No.32-1383), respectively. Fig. 3(c) shows the XRD pattern recorded from the surface of the sintered sample. Two phases of Ti_3SiC_2 and TiC appear, indicating that the formed TiC layer is not thick and the matrix material is also detected. The diffraction peaks for Ti_3SiC_2 haven't changed so much as compared (Fig. 3 (a) with Fig. 3 (c)), while these TiC have changed obviously as compared (Fig. 3 (b) with Fig. 3 (c)). The (220) peak for TiC becomes the strongest peak, while other peaks, especially (111) and (200) peaks, decrease dramatically in intensity, suggesting that the TiC platelet shape induces preferential orientations. A careful observation from Fig. 3 (c) reveals that the (111) and (222) peaks of TiC are still high. From Figs. 1 and 2, it can be found that most of the TiC platelets deposited with their basal planes perpendicular to the sample surfaces. Therefore, the greatly enhanced peak (220) indicates that the six side surfaces of hexagonal TiC platelets should be {110}, and the basal plane is (111).

In addition, the diffraction peaks for TiC shift to higher angles. For example, the diffraction angles 2θ for (111), (200) and (220) peaks change from 35.91°, 41.71°, 60.45° to 36.22°, 42.04°, 60.69°, respectively. This feature means that some Si and Al atoms have dissolved within the TiC lattice. The dissolved Si and Al atoms may occupy the Ti sites instead of C sites, because both Si and Al atoms are smaller than Ti atoms, while larger than C atoms. The dissolution of Si and Al into TiC

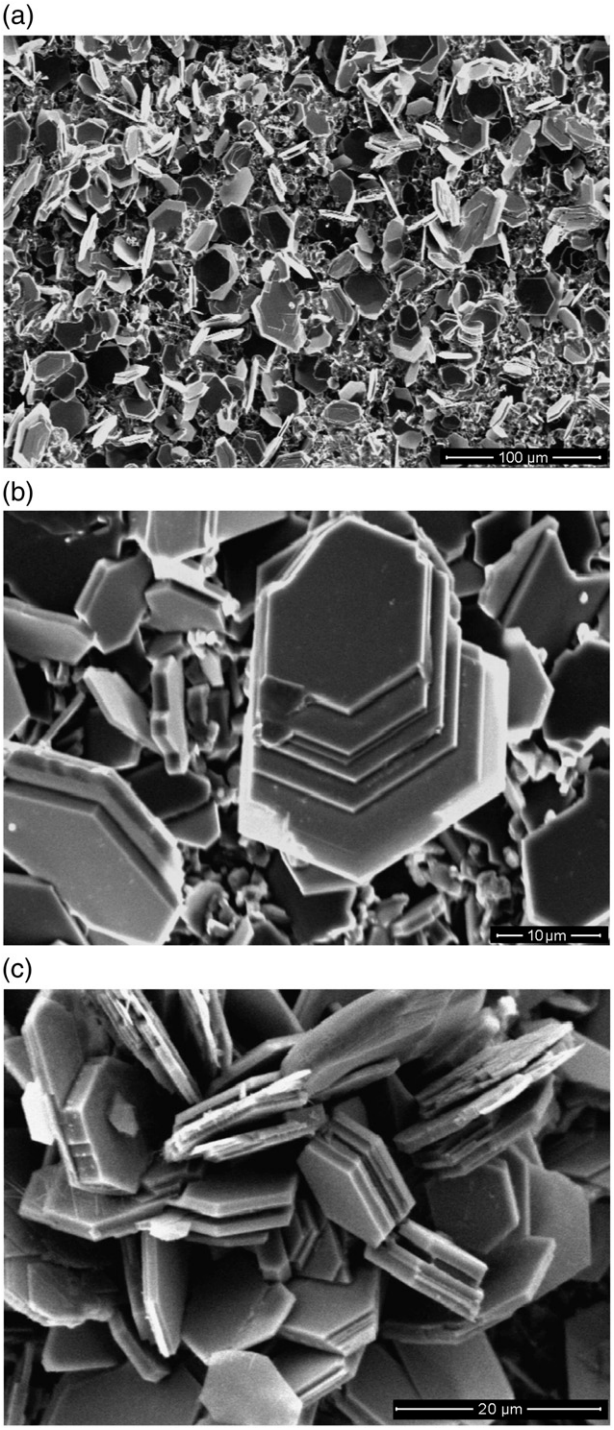

Fig. 1. A series of SEM micrographs of TiC platelets forming on the surface of the Ti/Si/TiC/$Al_{0.2}$ sample after sintering at 1450 °C for 10 min in an Ar atmosphere. (a) A low magnification; (b) and (c) high magnifications.

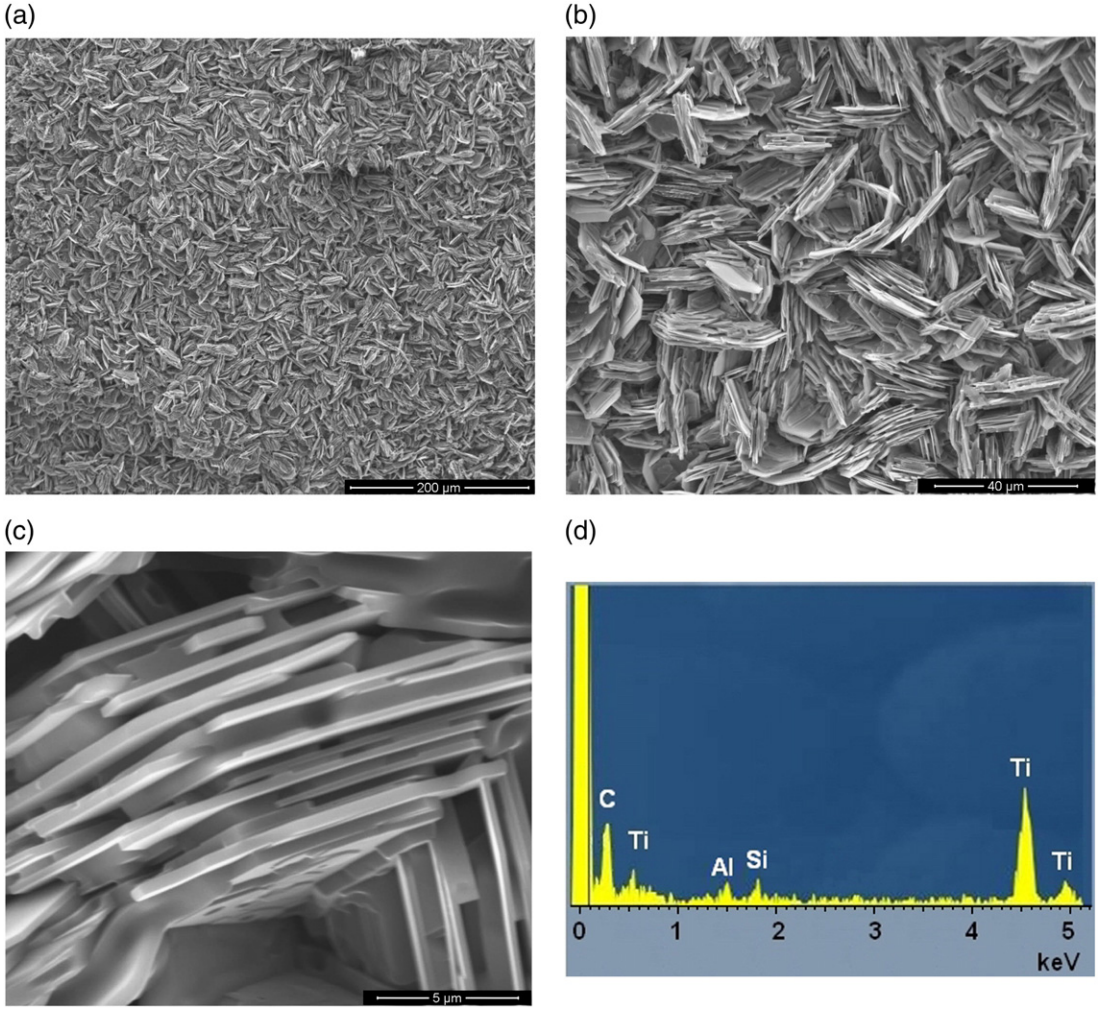

Fig. 2. A series of SEM micrographs of TiC platelets forming on the surface of the Ti/Si/TiC/$Al_{0.2}$ sample after sintering at 1500 °C for 10 min in an Ar atmosphere. (a) A low magnification; (b) and (c) high magnifications; (d) EDS spectra from the TiC platelets.

will reduce the lattice parameter of the TiC crystal structure. Therefore, according to Bragg's equation, $2d\sin\theta = n\lambda$, the Bragg angle will increase.

3.2. Growth mechanism of the TiC platelets

TiC is a typical faceted crystal. Fig. 4(a) shows its crystal structure. C atoms occupy the octahedral positions. If viewed along the direction perpendicular to the (111) planes, Ti and C atoms form a hexagonal shape as shown in Fig. 4 (b). It has been reported that TiC has a simple-hexagonal structure, but its hexagonal crystalline has never been observed [12]. Chien et al. [13] reported that stress induced the transformation of TiC from cubic to hexagonal structures.

In the present study, crystal structure, presence of impurities and growth conditions all influence the formation morphology of TiC. Small amounts of Al and Si elements dissolving into the TiC crystal structure can induce high density of defects (dislocations and stacking faults) in the TiC grains. It has been reported that the presence of impurities in TiC, such as boron, Si and Al, induced high density of planar defects within the TiC grains [11,14,15]. Therefore the high density of defects has significant influences on the structure of TiC and may promote the formation of TiC hexagonal platelet nuclei. In addition, under liquid condition free from restriction, the TiC nuclei are easily to form hexagonal platelets. Furthermore, it is well known that the crystalline shape is determined by the relative growth rate on the different planes. If the growth rate on the TiC (111) facet is slow, while on the {110} side facets is fast, a well-developed hexagonal TiC platelet forms.

According to the above results and observations, the TiC platelets should form from a reaction between Ti and C through the solution-precipitation mechanism. The source of C may originate from the used graphite dies. To confirm the above postulation, the Ti/Si/$Al_{0.2}$ sample without TiC was sintered at the same condition as that for Ti/Si/TiC/$Al_{0.2}$. It is found that a lot of TiC platelets also form on the sample surface, as shown in Fig. 5. This evidence further approves that the graphite dies provide the source of C, which reacted with Ti on the sample surfaces, forming the TiC platelets.

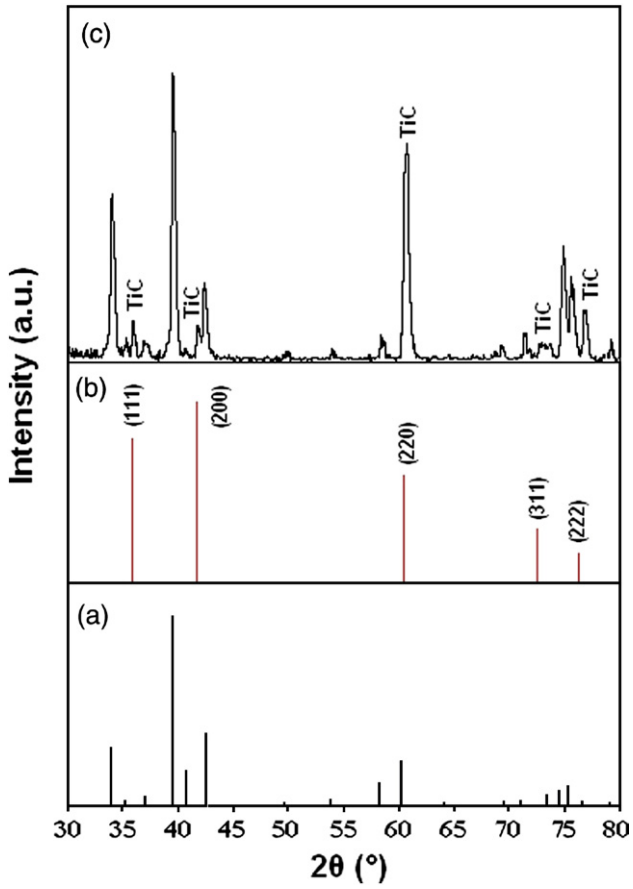

Fig. 3. (a) and (b) Standard XRD patterns of Ti_3SiC_2 and TiC, respectively; (c) XRD pattern recorded from the surface of the Ti/Si/TiC/$Al_{0.2}$ sample after sintering at 1450 °C for 10 min in an Ar atmosphere. In (c), unmarked peaks belonging to Ti_3SiC_2.

A growth mechanism shown in Fig. 6 has been proposed to explain the formation of the hexagonal TiC platelets.

During sintering of the above-mentioned samples, once the temperature exceeds the melting point of Al (660 °C), molten Al spreads everywhere, especially to the sample surface. Ti atoms can dissolve in the Al liquid. At high temperature, C atoms from the graphite dies diffuse rapidly to the sample surface and

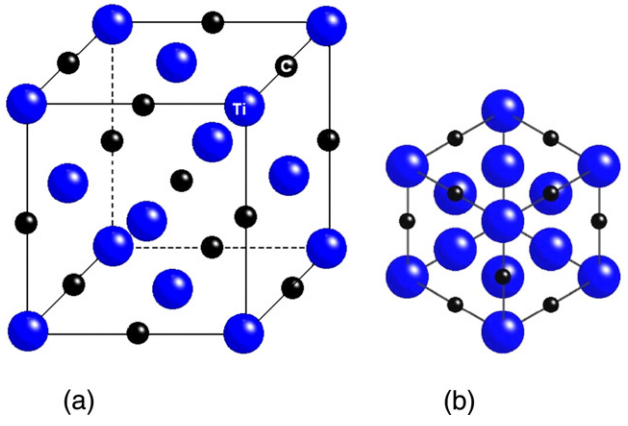

Fig. 4. (a) Crystal structure of TiC, and (b) projection of Ti–C atoms along [111] direction. The smaller atoms are C atoms.

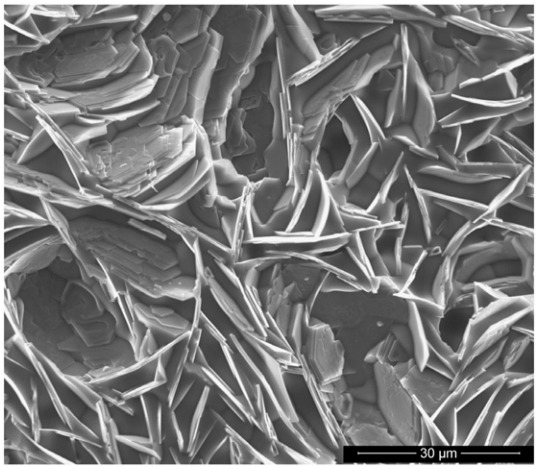

Fig. 5. SEM micrograph of TiC platelets forming on the surface of the sample made of Ti/Si/$Al_{0.2}$ after sintering at 1450 °C for 10 min.

dissolve in the Al liquid, in which Ti reacts with C to form TiC nuclei with a hexagonal shape (Fig. 6). The TiC nuclei will grow under the liquid condition on the sample surface free from restriction, finally forming a well-developed hexagonal platelet with a (111) basal plane (Fig. 6). As the temperature exceeds to 1333 °C, the other Ti–Si liquid forms, because the Ti–Si system exhibits two eutectic reactions for the Si–$TiSi_2$ and Ti–Ti_5Si_3 compositions, both at a temperature of 1333 °C [16]. Hence, the hexagonal TiC nuclei grow in the liquid all along. If the first hexagonal TiC platelet nucleus starts to form, on which the newly arrived Ti atoms and C atoms will continue to deposit and react to form the second TiC nucleus. With this process repetition, the stacking hexagonal TiC nuclei will grow together in the liquid condition. Each TiC nucleus grows a thin platelet. Finally, a thick hexagonal TiC platelet forms (Fig. 6).

The formation of TiC platelets on the sintered sample further explains the reason why impurity of TiC is always found in Ti_3SiC_2 and Ti_3AlC_2 powders. The main reason should be attributed to the fact that the diffuse of C from the graphite dies into a sample changes a designed composition, resulting in Ti-loss and forming surplus TiC in the reaction system.

4. Conclusion

A large amount of TiC hexagonal platelets has formed on the surface of the samples made of Ti/Si/TiC/$Al_{0.2}$ after sintering at above 1450 °C in an Ar atmosphere. The detailed structure shows that the TiC thick platelets are composed of thin platelets. The basal plane of TiC platelets is the (111) facet and side surfaces are {110} facets. The TiC hexagonal platelets form from a reaction between Ti and C through the solution-precipitation mechanism. A small amount of Al and Si elements dissolving into the TiC crystal structure has an effect on the formation of hexagonal TiC platelets.

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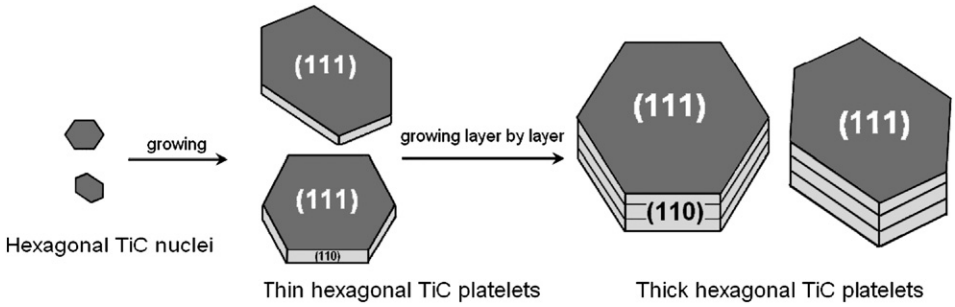

Fig. 6. Scheme of the growth process of the hexagonal TiC platelets.

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