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In situ growth of TiC whiskers in Al_2O_3 matrix for ceramic machine tools

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Abstract

TiC whiskers have been synthesized via a carbothermal reduction technique in an α-Al_2O_3 matrix within a temperature range of 1380–1580 °C in an argon atmosphere. The raw materials consist of TiO_2, carbon, nickel and NaCl. Various mixing procedures and reaction temperatures were used. The yield of the whiskers is mainly dependent on the mixing procedures and the morphology of the synthesized composite powders is mainly dependent on the synthesis temperatures. The majority of the synthesized whiskers display an ideal aspect ratio of 10–30 with a diameter of 1–3 μm. No significant influence on the growth of the TiC whiskers by the present of the Al_2O_3 matrix powder can be noted.

Keywords: TiC whisker; α-Al_2O_3; Carbothermal reduction; In situ growth; Mixing procedure

1. Introduction

Moderate quantity of whiskers with high elastic modulus as an additive can greatly improve the flexural strength and fracture toughness of ceramic materials [1]. However, the application of whiskers is still limited by such disadvantages as healthy hazard, difficult dispersion, a high cost, etc. In situ growth of whiskers in a matrix material is a promise way to overcome such disadvantages. Two patents of in situ growth SiC whiskers strengthen Al_2O_3 and Si_3N_4 have been, respectively, reported in Japan [2]. However, SiC whiskers have a lower thermal expansion coefficeint and somewhat poor chemical stability. As a result, the pull-out effect in Al_2O_3/SiC whisker composites may be weakened by a thermal stress introduced by the mismatch of their thermal expansion coefficients. And cutting tools made by such composites are generally used to cut Ni alloys instead of ferrous metal because of the reaction between the compound SiC and element Fe in ferrous metal. TiC particles are commonly used as an additive in Al_2O_3 matrix composite cutting tool materials [3] because of the ideal physical compatibility and the chemical stability between the compound TiC and element Fe. However, the application of TiC whiskers is limited not only by such disadvantages as discussed above, but also by high cost. In situ growth of TiC whiskers strengthening and toughening Al_2O_3 matrix composite tool materials can greatly reduce the cost and environment pollution by such advantages as the direct synthesizing the whiskers in a matrix material and avoiding the complicated mixing procedures. On the other hand, some special microstructure introduced by the in situ growth procedure and some controllable byproducts or remnants such as Al_2TiO_5 and carbon may lead to new composites with some excellent mechanical properties. However, few reports on in situ growth of TiC whiskers in any matrix material can be currently noted.

TiC whiskers can be prepared via either a chemical vapor deposition (CVD) method [4–7] or a carbothermal reduction technology [8–11]. The CVD method is more frequently used to explore new whiskers. However, the carbothermal reduction technology is more economical and more frequently used in large-scale commercial productions, for example, the SiC whiskers. Moreover, considering to obtain a composite powder with a homogeneous distribution of whiskers in a matrix is a critical problem in such researches as in situ growth processes, the carbothermal reduction technology is used in our work. TiO_2, carbon and NaCl are used as the raw materials and Ni as the catalyst. Three different mixing procedures and a synthesis temperature range of 1380–1580 °C are tested. The yield and

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morphology of the synthesized TiC whiskers in the Al_2O_3 matrix under different experimental conditions are studied.

2. Experimental procedure

Commercial TiO_2, amorphous carbon, Ni and chemically pure NaCl are used as precursors. Commercial α-Al_2O_3 with an average grain size of 0.5 μm is used as the matrix material. The molar ratio of TiO_2:C:NaCl:Ni is 1:3:0.5:0.05. The synthesized composite powders are theoretically calculated to contain about 30 vol% TiC and the actual fractions of the whiskers synthesized in the various experimental conditions are compared and analyzed by the scanning electron microscope (SEM) photographs. The precursor mixtures, respectively, named as AT300, AT301 and AT302, are mixed by three different procedures. AT300 is mixed in a blender for 30 min and sieved through a 100-mesh sieve for two times, and then sieved through a 200-mesh sieve for another two times. AT301 is prepared by a dry ball milling procedure for 24 h, and then sieved though a 100-mesh sieve. AT302 is dispersed for 30 min by a supersonic vibration in ethanol medium and ball milled for 24 h, then dried in a vacuum dry box and sieved through a 100-mesh sieve. Each 15 g of the mixed powders is, respectively, put into a graphite reactor with several small holes on the lid to allow gas exchange between the reactor and the surrounding atmosphere, heated to the synthesis temperature in 10–12 min in a flowing argon-gas atmosphere and held for 90 min duration time. The various synthesis temperatures are, respectively, 1380, 1480 and 1580 °C.

The obtained phases are characterized by a power X-ray diffractometry (XRD). The yield and morphology of the whiskers are investigated by a SEM (Hitachi S-570 SEM).

3. Results and discussion

3.1. Characterization of obtained mixture

The XRD pattern of the synthesized composite powders with different mixing procedures and react temperatures are shown in Fig. 1. No TiO_2 can be detected by the XRD and TiC is

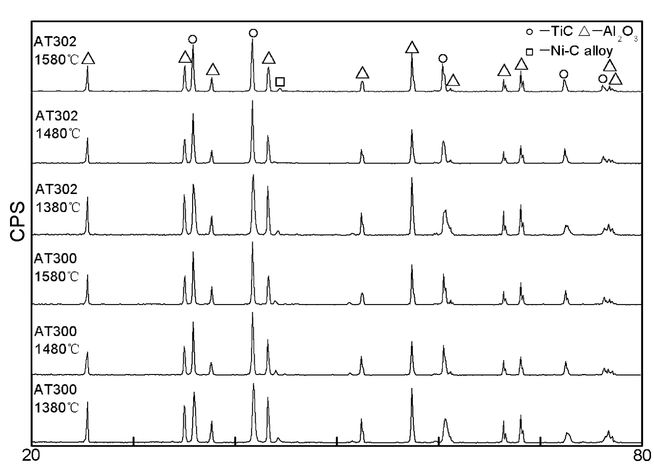

Fig. 1. XRD of the synthesized composite powders.

successfully synthesized. Whiskers can be observed distributed among the Al_2O_3 matrix grains shown in Fig. 2. The majority of the whiskers display an ideal aspect ratio of 10–30 with a diameter of 1–3 μm and a smooth surface shown in Fig. 3(a). No obviously agglomeration of the whiskers can be noted, while some agglomeration and growth of the Al_2O_3 matrix grains can be observed shown in Fig. 3(b). Some clusters of superfine powder with a nano-scale diameter can be observed either among the alumina grains or adhere to the synthesized whiskers shown in Fig. 3(a and c). Such clusters of powder are thought to be the carbon remnants. It can be summarized that the yield of the whiskers is mainly dependent on the mixing procedures and the morphology of the synthesized composite powders is mainly dependent on the synthesis temperatures, which will be discussed below.

3.2. Yield of the TiC whiskers

Different mixing procedures can obviously influence the yield of the whiskers while the mechanism is still not clear [9]. However, to maximize the yield of the whiskers, such three factors combined with the mixing procedure can be summarized as a good dispersed homogeneous mixture, improving the mass transport and avoiding the direct reaction between TiO_2 and carbon during the synthesizing process. In the carbothermal reduction technology, the growth of the TiC whiskers is via a precipitation from the Ni–C alloy droplets. The direct reaction between TiO_2 and carbon will lead to the form of TiC particles instead of whiskers [9].

The influence of the mixing procedure on the yield of the TiC whiskers are compared by the SEM photographs shown in Fig. 2. It can be noted that the maximum yield of the TiC whiskers is obtained in AT300, which is mixed by a blender and sieves. Such a procedure can avoid the escape of the volatile compositions in the carbon. The carbon containing a large amount of volatile compositions can improve the mass transport in the synthesis process, and then lead to a high yield of the TiC whiskers [9]. Lower yield is obtained in AT302, which is dispersed for 30 min by a supersonic vibration in ethanol medium and ball milled for 24 h. Such a procedure can obtain a good dispersed homogeneous mixture. However, some volatile compositions might escape during the dry process and the high-speed ball milling procedure will enhance the active of the particles and improve their contact condition, which is somewhat similar to the mechanical alloying (MA) effect and may be named as a ball milling (BM) effect. Such an effect will be beneficial to the direct reaction of TiO_2 and carbon. The lowest yield is observed in AT301, which is mixed by a dry ball milling procedure. Volatile compositions may escape because of the heat introduced by friction, and the BM effect will be obviously enhanced by such a mixing procedure.

It is found that the synthesis temperature has no obviously effect on the yield of the whiskers in AT300. However, apparently lower yield of the whiskers can be observed in AT301 and AT302 synthesized at 1580 °C shown in Fig. 2, indicating that a BM effect is working and such an effect can be obviously enhanced at a higher synthesis temperature.

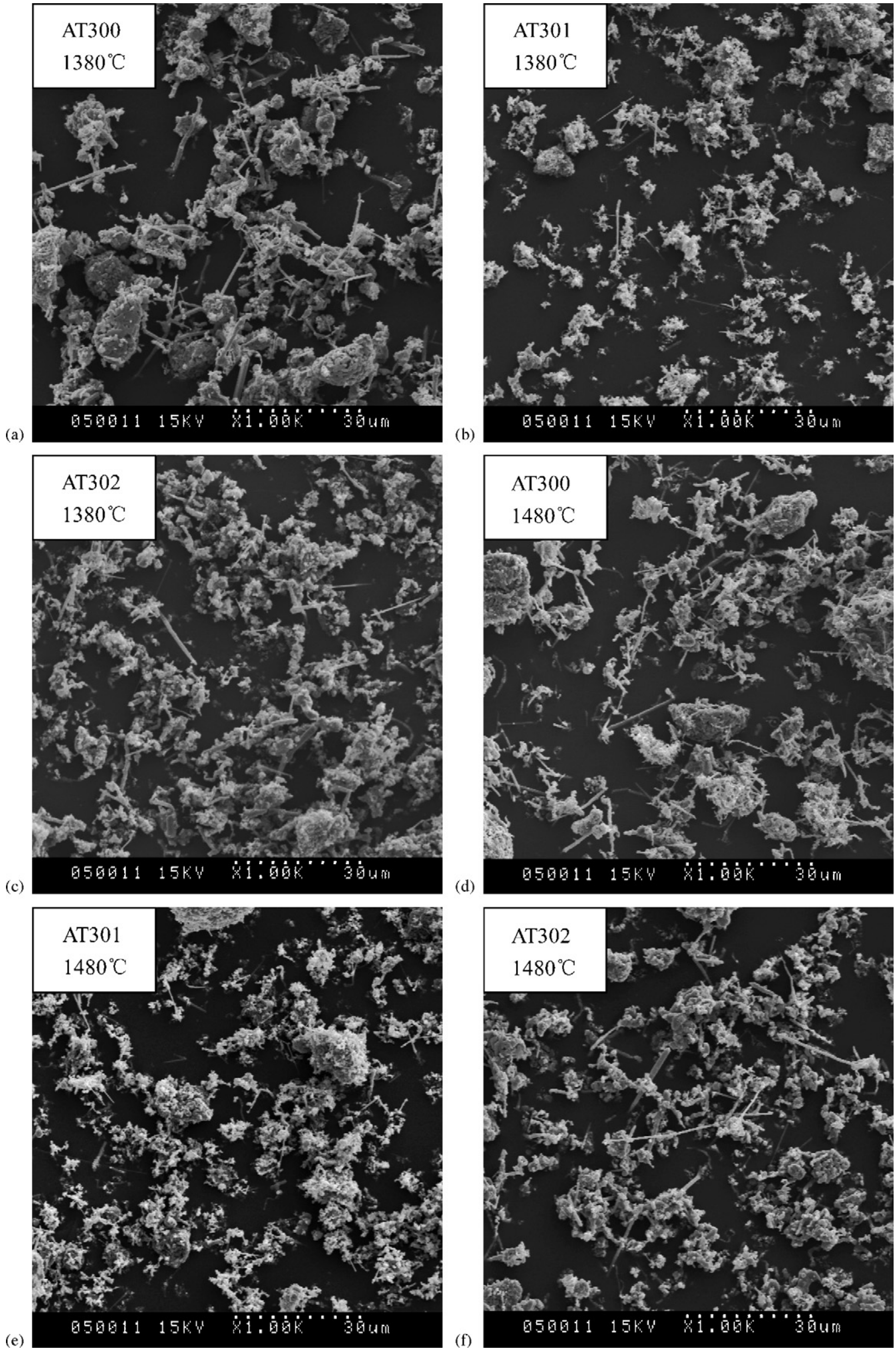

Fig. 2. (a–i) Yield of whiskers at different experimental conditions.

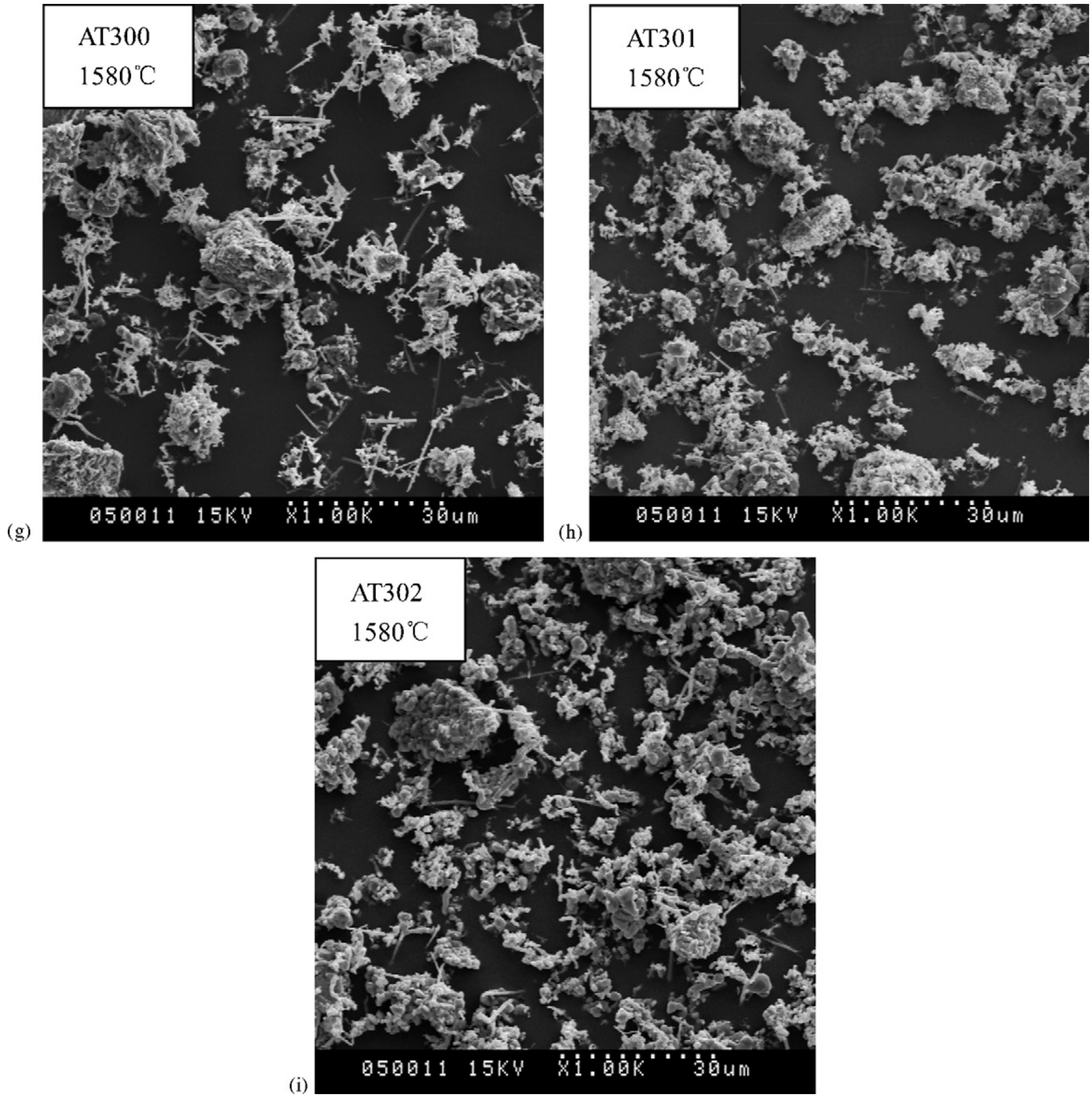

Fig. 2. (*Continued*).

3.3. Morphology of the mixture

The morphology of the mixture is mainly dependent on the synthesis temperature. Some whiskers with a square cross-section and a rough axial surface can be observed in the composite powders synthesized at 1380 °C shown in Fig. 3(c), whereas only round and smooth whiskers can be found at a higher synthesis temperature such as 1480 and 1580 °C. Such results as the influence on the yield of the whiskers by the mixing procedures and the influence on their morphology by the synthesis temperatures are consistent with the details discussed by Ahlen et al. [8,9], indicating that there is no significant influence on the growth of the whiskers by the present of the alumina matrix powder.

Due to the present of Al_2O_3 powder, no obviously agglomeration of the whiskers can be noted. However, agglomeration and growth of the matrix grains can be observed shown in Fig. 3(b). Obviously growth of the matrix grains can be observed in the products synthesized at 1480 °C. Some of them can grow from the origin 0.5 to 3–4 μm when the synthesis temperature is elevated to 1580 °C. Severe matrix grain agglomeration can be observed in AT300 shown in Fig. 2, indicating a poor dispersion of the raw mixture.

3.4. The influence of the matrix Al_2O_3 powder

Before the experimental in situ growth of the TiC whiskers, it has been observed by the experiments of in situ growth of TiC_xN_{1-x} whiskers in Al_2O_3 matrix that a carbothermal reduction process of the Al_2O_3 can also take place. AlO is detected at 1250 °C and AlN is at 1550 °C on the XRD pattern. However, there is no other compounds except for the synthesized TiC, the alumina matrix and some Ni–C alloy can be noted on the XRD patterns of in situ growth of TiC whiskers, indicating that α-Al_2O_3 is stable in the argon-gas atmosphere at the synthesis temperatures and will not participate in the carbothermal reduction process.

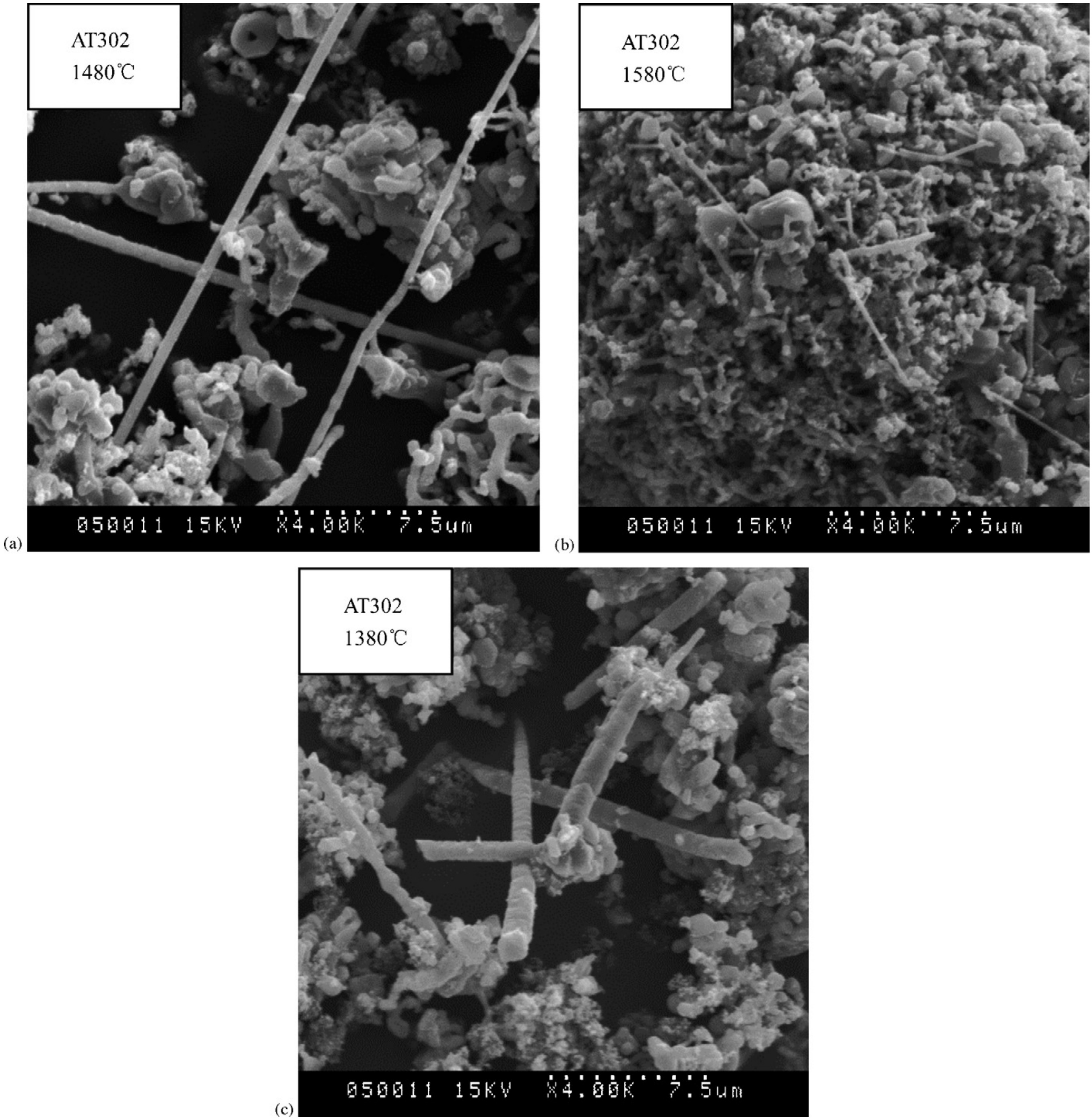

Fig. 3. (a–c) Morphology of the whiskers and grains.

3.5. The carbon remnants

TiC is a non-stoichiometric compound where the atomic fraction of C can change from 0.32 to 0.5. The compound TiC with a high atomic fraction of C such as ~0.5 is difficult to be synthesized, and then the carbon remnants can hardly be avoided when a stoichiometric amount of carbon has been used in our work. However, the carbon used in the work is with an amorphous phase, which is difficult to be detected by the XRD patterns whereas can be observed by the SEM photographs shown in Fig. 3(a and c). It has been reported [3] that the fracture toughness of Al_2O_3/TiC ceramic material can be increased by a moderately added amount of carbon. However, such clusters of the carbon remnants as shown in Fig. 3(c) will certainly decrease the dense and mechanical properties of the sintered composite. So the amount of the carbon remnants in the synthesized composite powder must be controlled. To decrease the added amount of carbon may be one of the methods to avoid the excessive carbon remnants. However, such a method may also decrease the atomic fraction of C in the TiC whiskers. It seems from our experimental results that the amount of carbon remnants can be decreased when the synthesis temperature is elevated. However, growth and agglomeration of the matrix grains can also become severe.

4. Conclusions

The TiC whiskers have been successfully synthesized in an Al_2O_3 matrix. The majority of the whiskers have an ideal aspect ratio of 10–30 with a diameter of 1–3 μm. The yield of the whiskers is mainly dependent on the mixing procedures and the morphology of the mixtures is mainly dependent on the synthesis temperatures. The maximum yield of the whiskers can be obtained in a raw material mixed by a blender and sieves and smoothly round whiskers can be obtained at a higher synthesis temperature of 1480 and 1580 °C.

No significant influence of the present of α-Al_2O_3 matrix powder on the growth of the TiC whiskers can be noted. Thus, the α-Al_2O_3 is stable at the synthesis temperatures when the whiskers are grown in an argon-gas atmosphere. Clusters of carbon remnants can be observed on the SEM photographs, the amount of which should be controlled.

Acknowledgements

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