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Synthesis of TiB_2+ TiC by mechanical alloying ①

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[Abstract] The process of the mechanical alloying reaction between B_4C and Ti during ball milling was studied by EPMA and X-ray diffraction. It is revealed that the reaction of $3Ti+ B_4C= 2TiB_2+ TiC$ can be induced by mechanical alloying within 90 min of ball milling. The XRD peaks of TiB_2+ TiC are broadened with increasing ball milling time.

[Key words] TiC; TiB_2; mechanical alloying
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1 INTRODUCTION

TiB_2 and TiC are both stable compounds with certain of the characters of metals (luster, conductivity, etc). They have extraordinary hardness, excellent resistance to abrasion and erosion, so they are very useful non-oxide ceramic. They are often utilized to fabricate ceramic-based superhard alloying and high strengthened and conductive metal-based composite materials in which TiC and TiB_2 are taken as strengthened-phase. They have been received extensive attention due to their excellent performance abroad or at home.

Although they have the above merits, their high price affects their application because raw materials of synthesis of TiB_2 and TiC are costly and their preparation technics are comparatively complex. At present, exploring emphases all over the world is the synthetic method of TiC and TiB_2 powders with high quality (content> 98%), fine particles (average particle diameters< 1 μm) and low price. TiC + TiB_2 composite powders have also respective characters so they have powerful utilization in industry.

Reactive milling technique has been used to chemical refining of metals by McCormick et al[1]. Milling with C and CuO, the as-milled product consists of pure Cu and a reaction by-product of CO_2 which is easy to discharge. Milling with $TiCl_4$ and Mg, Ti powders and by-products of $MgCl_2$ and unreacted Mg can be attained. The mechanical solid-state reaction of CuO-Ti system has been investigated by El-Eskanderany et al[2]. Studying reports on synthesis of TiB_2 + TiC composite powders by reactive milling have not been published abroad or at home. In this paper, the process of the mechanical alloying reaction between B_4C and Ti during ball milling is studied. The products of TiB_2+ TiC is also analyzed.

2 EXPERIMENTAL

Milling process was performed at room temperature in a GN-2 ball mill equipped with GCr15 steel vial and balls with diameter of 10 mm. Ti (< 74 μm) and B_4C (< 147 μm) powders of nominal purity of 99% were mixed to be used as starting reactant materials according to stoichiometric ratio of 3∶1. The powders were sealed under argon atmosphere (99.99%) protecting oxidation from milling. The structural evolution of mechanically alloyed powders were determined by means of XRD with Cu K_α in a RIGAKU D/max-3b X-ray diffractometer. Morphology changes of the products were viewed and analyzed in a RIGAKU EPMA-8705 and EPMA-1600 electron microanalyzer.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

Fig. 1 shows the changes in XRD patterns of a powder mixture (Ti + B_4C) at different milling times. The sharp diffraction peaks of TiB_2 and TiC composite powders appear and the diffraction peaks of Ti and B_4C disappear after milling 90 min, as shown in Fig. 1(a). It implies that Ti and B_4C have taken place the reaction of $3Ti+ B_4C= 2TiB_2+ TiC$. So the synthesis of TiB_2 + TiC can be performed through milling at room temperature. If Cu was mixed with the above reactant materials, the reaction did not take place until 930~ 970 ℃ when the content of Cu reach 80% (mass fraction)[3]. In general, the reactive mechanism of mechanical alloying is classified into two categories[1~ 11], one is gradual interdiffusion reaction of interface atoms, the other is mechanically induced self-propagating reaction. The formation time of TiB_2+ TiC is only 90 min, moreover, the

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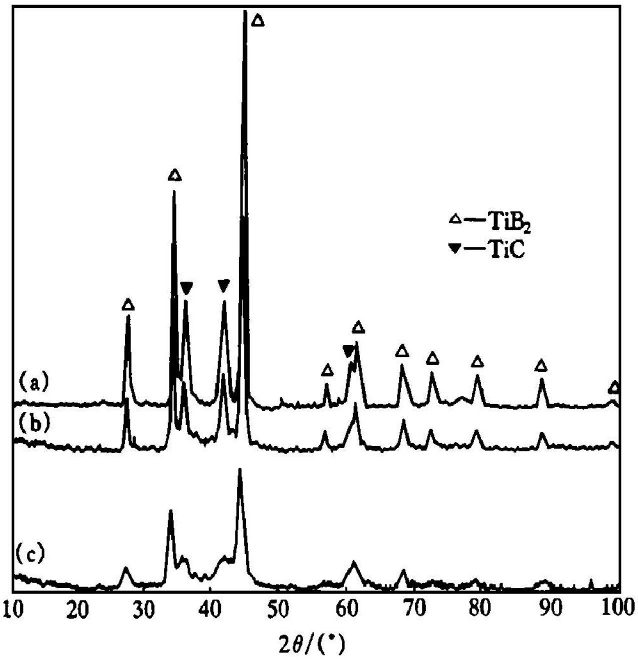

Fig. 1 X-ray diffraction patterns of powders milled for different time
(a) —90 min; (b) —120 min; (c) —600 min

diffraction peaks of Ti and B_4C did not appear. It is such short time during room temperature milling that the diffusion reaction is very difficult to occur. By calculation, the reactive adiabatic temperature can reach 3 193 K (melting point of TiB_2), it is much higher than 1 300 K, which is critical temperature of the occurrence of MSR[5, 10], so we think the reactive mechanism is the second. The grain sizes decreased and reactive interface areas increased during powder-milled in a high-energy ball mill. Fracture of particles created atomically clean surface and local temperature rose, result in and promote interdiffusion due to changes of structural parameters and enhancing of dislocation density. This can induce the occurrence of self-propagating reaction. With further milling, the diffraction peaks became broad. An amount of grain strain and dislocation was introduced into powders in the course of repeated collision of ball-powder-ball. The phenomenon of the diffraction broadening will be further investigated and analyzed in detail in subsequent work.

3.2 EPMA morphology analysis

Fig. 2 shows the second electron images from powders at various times. The surface of all powders

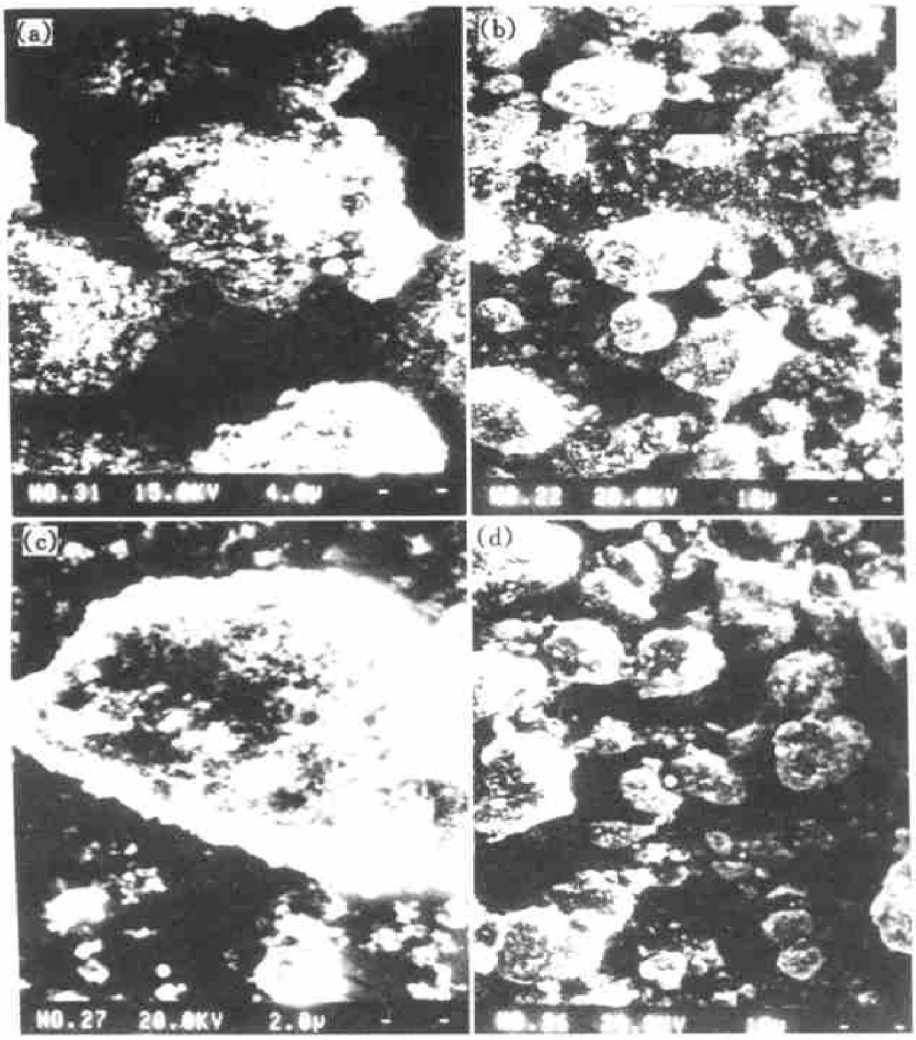

Fig. 2 Morphologies of powders milled for different time
(a) —90 min; (b) —240 min; (c) —600 min; (d) —600 min

has a sponge-like appearance. It indicates morphology of powder particles changed little in the range of as-milled times. Only the grain sizes were affected. This has also been testified through XRD analysis. After milling 90 min, TiB_2 and TiC was formed. In subsequent milling, the phase structure and particle diameters of the product were rarely affected. The average diameter of the large particles is approximately 10 μm in Figs. 2(b), (c). The large particles are composed of much finer particles and numbers of small cavities in Figs. 2(a), (c). Because the reactive mechanism of Ti and B_4C is mechanically induced self-propagating reaction, too high reaction rate engendered gas rapid formation and discharge that powder particles formed many cavities. When grain sizes decreased, the powders having high energy can result in aggregation of the fine particles.

4 CONCLUSIONS

1) The reaction of $3Ti + B_4C = 2TiB_2 + TiC$ can take place after milling 90 min.

2) With further milling, the diameters of the composite powder rarely change but the crystallic sizes decrease gradually.

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