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ScienceDirect
Journal of the European Ceramic Society 29 (2009) 181–185
www.elsevier.com/locate/jeurceramsoc

Low-temperature synthesis of high-purity Ti_3AlC_2 by MA-SPS technique

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Received 8 December 2007; received in revised form 21 April 2008; accepted 2 May 2008
Available online 11 July 2008

Abstract

Ternary carbide Ti_3AlC_2 was synthesized by mechanical alloying (MA) and spark plasma sintering (SPS) from elemental powder mixtures of Ti, Al and C, and the effect of Al content on formation of Ti_3AlC_2 during both processes was investigated. The results showed that adding proper Al content in the staring materials significantly increased the phase purity of Ti_3AlC_2 in the synthesized samples. Dense and high-purity Ti_3AlC_2 with <1 wt.% TiC could be successfully obtained by spark plasma sintering of powders mechanically alloyed for 9.5 h from a starting powder mixtures of 3Ti/1.1Al/2C at a lower sintering temperature of 1050 °C for 10–20 min.

Keywords: Ti_3AlC_2; Carbides; Sintering; X-ray methods

1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) is a promising advanced ceramic belonging to a member of the so-called "312" ternary carbides material group (i.e. Ti_3SiC_2, Ti_3AlC_2, Ti_3GeC_2).[1] It has a unique combination of the properties of both metals and ceramics including good electrical and thermal conductivity, high strength and modulus, high thermal shock, high-temperature oxidation resistance, low density, and being machainable with conventional high-speed tools without lubrication. In addition, in contrast to the normal brittle ceramics, Ti_3AlC_2 exhibits some abnormal room-temperature compressive plasticity.[2–4] Due to above excellent properties, the applications of this material are very potential. For example, it can be used as a high-temperature structural material, and also to process abrasion-resistant components and rotating parts, and so on.

In the past decades, a variety of sintering methods were used to synthesize Ti_3AlC_2. Pietzka and Schuster [2] first synthesized Ti_3AlC_2 by sintering cold-compacted powder mixtures of Ti, TiAl, Al_4C_3, and carbon under hydrogen for 20 h. In addition, such as hot isostatic pressing (HIP),[3] hot pressing (HP),[4–7] pressureless sintering (PS),[8] self-propagating high-temperature synthesis (SHS)[9–11] and spark plasma sintering (SPS)[6,12–14] have also been adopted to synthesize Ti_3AlC_2. However, higher synthesis temperatures (>1200 °C) were required in these methods. Mechanical alloying (MA) is a conventional and convenient powder metallurgy process with low fabrication cost. It is one of the most promising technologies for obtaining compounds at room temperature. Recently, Ti_3AlC_2 phase was found by MA in Ti–Al–C system.[15] However, in their report, TiC was still the main phase in synthesized products, with a small amount of Ti_3AlC_2 and Al_3Ti. This indicates that high-purity Ti_3AlC_2 is difficult to synthesize via mechanical alloying alone. On the other hand, basic research and industrial applications of MA powder need the consolidation of powder for the structural materials. Spark plasma sintering, which is also called pulse discharge sintering (PDS),[16] is a novel sintering method to synthesize metallic or ceramic compound. It can rapidly consolidate the powders to high density by applying pressure and passing electric pulse current within short soaking time owing to rapid heating and cooling rates. With the developments of material manufacturing technologies, mechanical alloying associated with spark plasma sintering (MA-SPS) is considered as

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doi:10.1016/j.jeurceramsoc.2008.05.035

an effective technique to prepare various materials. Some bulk compounds have efficiently been prepared by SPS of mechanically alloyed powders.[17,18] The main purpose of the present work is to fabricate a high-purity and dense Ti_3AlC_2 at lower temperature by spark plasma sintering of mechanically alloyed products from elemental powders of Ti, Al and C.

2. Experimental procedure

Commercially available Ti (average particle size: 80 μm, purity >99.36%), Al (average particle size: 50 μm, purity >99.6%) and graphite C (average particle size: 20 μm, purity >99.0%) powders were used as raw materials in this study. These powders were weighed according to the molar ratio of 3Ti/*x*Al/2C ($x = 1$, 1.1, 1.2). The powder mixtures were put in steel jars and sealed in a glove box under argon protective atmosphere. MA was conducted by swinging, high-energy ball mill, and the rotation speed of the milling containers was set as 400 rpm. The weight ratio of balls to powders was 10:1. The powders of MA for 9.5 h were sieved (100 mesh) and put in a cylindrical graphite die with an inner diameter of 10 mm and sintered by SPS. The heating rate was controlled at 80 °C/min and the sintering temperature was selected in the range of 900–1150 °C. The soaking time was 5–20 min and the constant axial pressure was 35 MPa in sintering process. After sintering, the surfaces of samples were ground to remove graphite layer.

The phase analysis of the MA powders and sintered bulks was identified by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation. The density of samples (ρ_M) was measured by Archimedes' method, and the theoretical density (ρ_T) was calculated by taking account of the theoretical density of TiC (4.9 g/cm^3), Ti_3AlC_2 (4.25 g/cm^3) and the weight percents of the two phases. The fracture surfaces of the sintered bulks were observed and analyzed by scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of the powders obtained by 9.5 h mechanical alloying of the starting composition of 3Ti/*x*Al/2C ($x = 1$, 1.1, 1.2). It can be seen that a large amount of Ti_3AlC_2 has been already formed by MA in Fig. 1(a) and (b). The TiC as impurity phase coexists with Ti_3AlC_2. However, with increasing of more Al content until $x = 1.2$ (see Fig. 1(c)), the peaks of Ti_3AlC_2 decreased in the intensity while the intensity of TiC increased. This suggests that excessive Al would suppress the formation of Ti_3AlC_2 during MA. The formation of the mechanically alloyed products may be attributed to a mechanically induced self-propagating reaction (MSR).[19] This MSR also was revealed in result reported by Li et al. [15] to synthesize Ti_3AlC_2 by mechanically induced self-propagating reaction in Ti–Al–C system. The MSR does not occur at the beginning of the ball milling stage. The process begins with an activation period or incubation, during which the mixed powders of Ti, Al and C undergo the repeated fracture and cold welding process, resulting in the refinement of particles and the formation of defects and internal strains. As the milled powders reached a

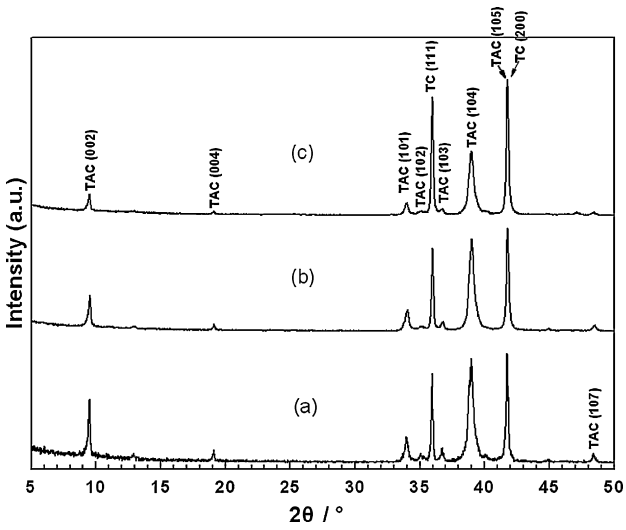

Fig. 1. XRD patterns of the powders formed by 9.5 h mechanical alloying of different starting mixtures: (a) 3Ti/1Al/2C, (b) 3Ti/1.1Al/2C and (c) 3Ti/1.2Al/2C. TAC and TC stand for the Ti_3AlC_2 and TiC, respectively.

defined critical size, the number of chemically active defect sites increases, the diffusion distance decreases and a large surface area forms, the MSR is ignited.

From the above results, it can be clearly confirmed that high-purity Ti_3AlC_2 is too difficult to obtain via mechanical alloying alone. So the powders formed by MA were subsequent spark plasma sintered. Fig. 2 shows XRD patterns of the as-sintered samples by spark plasma sintering of mechanically alloyed powders from 3Ti/1Al/2C powder mixtures at the temperatures ranged from 900 to 1150 °C for 5 min. It is seen that the sintered samples were composed of Ti_3AlC_2 and small amount of TiC as impurities, and no other phases were observed in XRD. This indicated a non-equilibrium structure of the ball-milled powder with TiC and Ti_3AlC_2 structure supersaturated with Ti and Al. The Ti_3AlC_2 peaks in the XRD of resultant samples significantly increased with the increase of sintering temperature. According

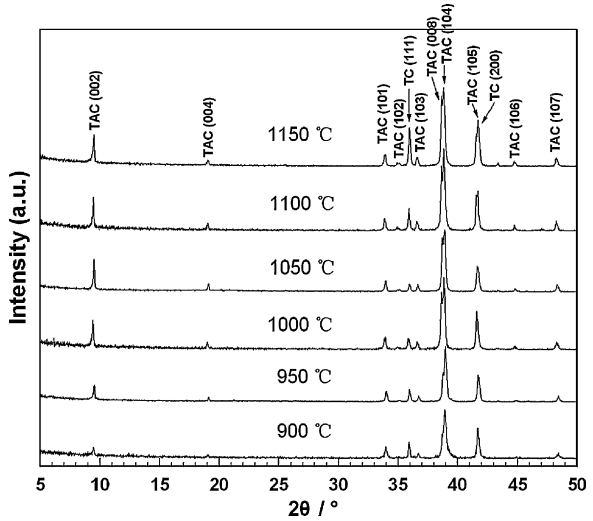

Fig. 2. XRD patterns of the samples sintered from mechanically alloyed powders of the starting composition of 3Ti/1Al/2C powder mixtures at different temperatures for 5 min.

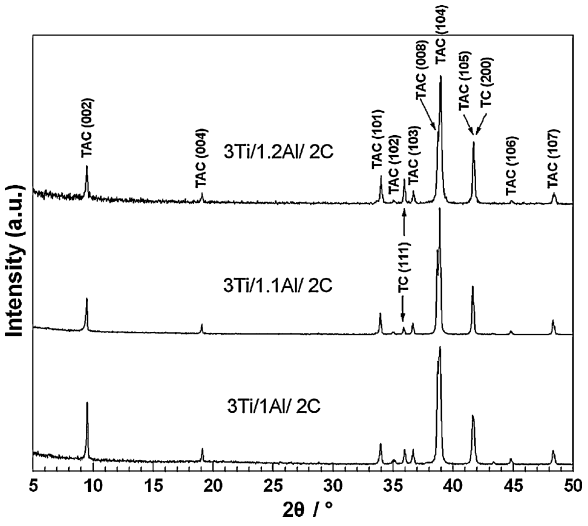

Fig. 3. XRD patterns of the samples sintered of MA powder with different Al content at 1050 °C for 5 min.

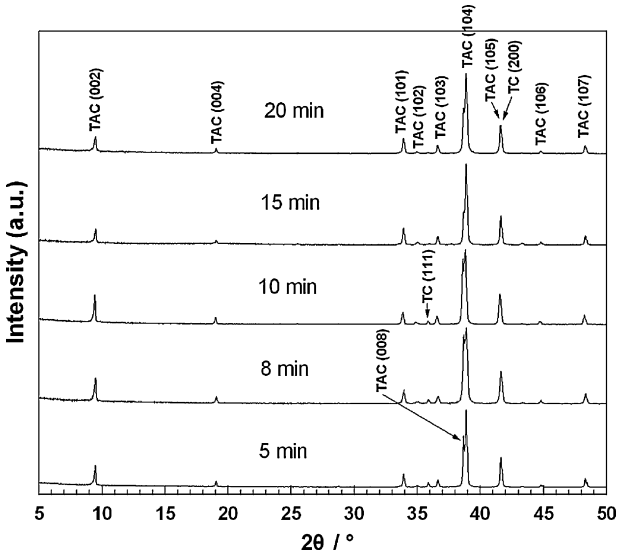

Fig. 4. XRD patterns of the samples sintered from mechanically alloyed powders of 3Ti/1.1Al/2C powder mixtures at 1050 °C for different holding times.

to Fig. 2, the (1 1 1) peak intensity of TiC at $2\theta = 35.9°$ reaches its lowest point at 1050 °C, suggesting that the relative content of TiC in these samples are lower than those in other samples. With the increasing of sintering temperatures from 1100 to 1150 °C, the intensity of TiC increases abruptly, indicating that Ti_3AlC_2 began to decompose to form TiC in this temperature range. The phenomenon of unstability of Ti_3AlC_2 synthesized by SPS was also found in result of Zhou et al. reported.[6] The reason why the decomposition of Ti_3AlC_2 at relative low temperatures may mainly be that local high temperature in samples, which is much higher than that of the thermocouple measured, was caused during instant discharging by SPS. Moreover, due to the evaporation of Al at relative high temperature, synthesized Ti_3AlC_2 decomposed into TiC because of the loss of Al. Thus, the thermal stability of Ti_3AlC_2 synthesized by SPS significantly lowers.

Furthermore, the MA powders were further sintered at 1050 °C for different Al content in order to reveal the effect of Al content on the relative content of TiC. As shown in Fig. 3, the XRD patterns of the samples from 3Ti/xAl/2C ($x = 1$, 1.1, 1.2) revealed that the intensity of TiC decreased and the intensity of Ti_3AlC_2 increased when the content of Al reached 1.1. When x increased to 1.2, the peaks of relative intensity TiC increased instead. Therefore, the appropriate x should be controlled at 1.1. In order to study the effect of holding times on the purity of Ti_3AlC_2, the MA powder from 3Ti/1.1Al/2C was sintered at 1050 °C for 5, 8, 10, 15 and 20 min, respectively. The relevant XRD patterns were shown in Fig. 4. However, since the intensity of TiC at holding time for 15–20 min was very weak and the comparison between different holding times was difficult.

In order to determine the purity of Ti_3AlC_2 quantitatively, the following equations were adopted[20] to estimate the weight percents of Ti_3AlC_2:

$$W_a = \frac{I_a}{I_a + 0.220I_b + 0.084I_c} \quad (1)$$

Herein W_a represents the weight percentages of Ti_3AlC_2 phase. I_a, I_b and I_c represent the integrated diffraction intensities of the Ti_3AlC_2 (0 0 2) peak ($2\theta = 9.5°$), Ti_2AlC (0 0 2) peak ($2\theta = 13.0°$) and TiC (1 1 1) peak ($2\theta = 35.9°$), respectively. It should be noticed that in sintering process, no Ti_2AlC phase was formed. Thus, $I_b = 0$. The purity of Ti_3AlC_2 in the sintered samples was calculated in this way and is summarized in Fig. 5. For the composition of 3Ti/1Al/2C, it can be seen that Ti_3AlC_2 purity has the highest value of about 97.34 wt.% at 1050 °C for 5 min in Fig. 5(a). However, for the composition of 3Ti/1.1Al/2C, Ti_3AlC_2 purity increased to 98.4 wt.% at 1050 °C for 5 min. In addition, Fig. 5(b) shows that the effect of holding time on Ti_3AlC_2 phase purity. Through extending the holding time at 1050 °C, the purity of Ti_3AlC_2 increased obviously. The lowest value of TiC content <1 wt.% was obtained at 1050 °C for 10–20 min.

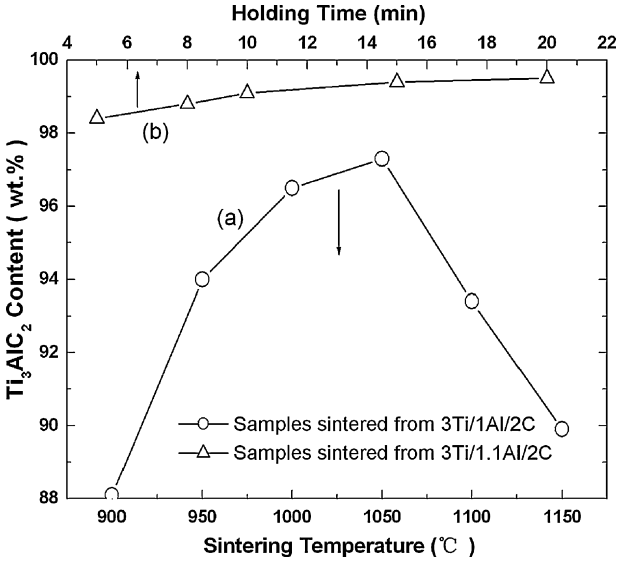

Fig. 5. (a) Ti_3AlC_2 purity in the samples sintered at 900–1150 °C for 5 min. (b) Ti_3AlC_2 purity in the samples sintered at 1050 °C for different holding times.

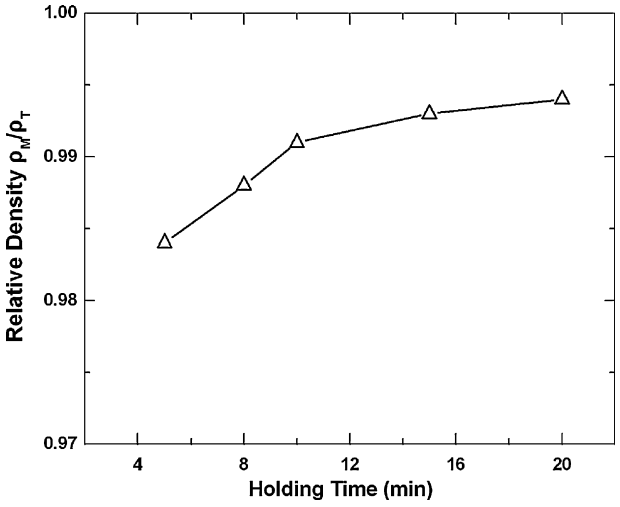

Fig. 6. The variation of relative density of the samples sintered from MA powder of 3Ti/1.1Al/2C at 1050 °C with holding time.

For the sintered samples, variation in relative density of the sintered samples from MA powder of 3Ti/1.1Al/2C with the holding time is shown in Fig. 6. The relative density ($\rho_R = \rho_M/\rho_T$) of the samples increases slightly with the increasing of the holding time. The relative densities were higher than 99% for the samples sintered at 1050 °C for 10–20 min.

Fig. 7 shows the SEM microstructure of the fracture surface of samples sintered from MAed powder of 3Ti/1Al/2C and 3Ti/1.1Al/2C at different temperature and time. In Fig. 7(a), for the sample sintered at 900 °C for 5 min, the structure is relatively loose and some little holes are observed. With increasing sintering temperature to 1050 °C, the samples become more dense and compact, as shown in Fig. 7(b). The microstructure of this sample consists of fine platelet grains, which are the typical characteristics of Ti_3AlC_2 ceramic. The platelet grains are about 0.1–0.3 μm in thickness and 3–10 μm in length. The effect of sintering time on microstructure is shown in Fig. 7(c) and (d). When the sintering time is 5 min, the average diameter is 5 μm. With extending sintering time to 20 min, the platelet grains were coarsened. The sizes of some grains could reach less than 0.5 μm in thickness and 10–20 μm in length, as shown in Fig. 7(d).

The present study shows that high-purity and dense Ti_3AlC_2 could be fabricated by spark plasma sintering of mechanically alloyed powder from 3Ti/1.1Al/2C at 1050 °C, and the sintering temperature of formation of high-purity Ti_3AlC_2 by MA-SPS was much lower than traditional single sintering methods, such as hot isostatic pressing,[3] hot pressing[4–7] and so on. Compared with other reports of Ti_3AlC_2 synthesized only by SPS,[6,12–14] the synthesis temperature decreased ≥150 °C. The following factors may be taken account for low-temperature synthesis of

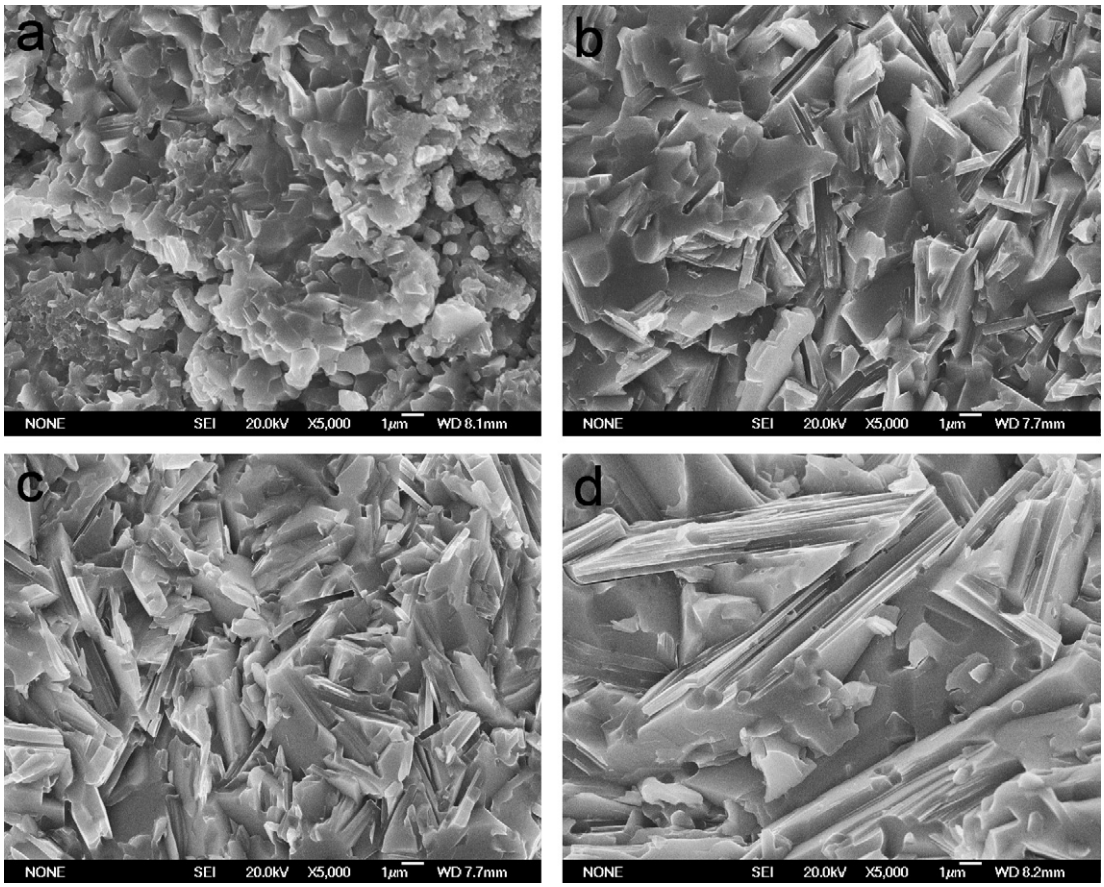

Fig. 7. SEM micrographs showing the microstructure of fracture surfaces: the samples sintered at (a) 900 °C and (b) 1050 °C for 5 min from mechanically alloyed powders of 3Ti/1Al/2C; the samples sintered at 1050 °C for (c) 5 min and (d) 20 min from mechanically alloyed powders of 3Ti/1.1Al/2C.

high-purity Ti_3AlC_2 by MA-SPS. One is the compound grains formed by MSR cannot grow rapidly because the reaction completed in very short time. Therefore, the fine grain sizes with large grain boundary areas, formation of defects and internal strains improved the sinterability, leading to a decrease in sintering activation energy and an increase in sintering driving force. Larger surface area and a large amount of grain boundary formed during MA provided a fast diffusion channel for atoms. These atoms had quite high diffusion velocity even at lower sintering temperature, and the related reactions could therefore occur. Moreover, a lot of fine Ti_3AlC_2 particles have been formed in the mechanical alloying mixed powders which can serve as crystal nuclei in the subsequent sintering process, promoting the transformation of the mixed powder into Ti_3AlC_2. Thus, MA powder can effectively reduce sintering temperature. On the other hand, in comparison with the synthesis technique using HIP[3] and HP,[5] one of the advantages of the spark plasma sintering technique itself has lower sintering temperature for the rapid synthesis of products.

4. Conclusion

In conclusion, high-purity Ti_3AlC_2 has been fabricated from Ti/Al/C mixtures by MA-SPS technique. Fully dense bulks Ti_3AlC_2 with high purity (>99 wt.%) were obtained at the relatively low temperature of 1050 °C for 10–20 min by spark plasma sintering of mechanically alloyed powders from the starting mixtures of 3Ti/1.1Al/2C.

Acknowledgements

This work was supported by Research Foundation for the Doctoral Program of Higher Education under Grant No. 20060183058 and Scientific and Technological Development Projects of Jilin Province in China under Grant No. 20070511.

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