Synthesis of high-purity Ti_2AlC by spark plasma sintering (SPS) of the elemental powders

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Recently, the layered ternary carbide Ti_2AlC has received considerable attention since it is a remarkable material that combines many of the best attributes of both metals and ceramics [1]. Like metals it is an excellent electrical and thermal conductor, easily machinable, relatively soft, not susceptible to thermal shock and it behaves plastically at higher temperatures. Like ceramics it is oxidation resistant, refractory and has a high strength, high melting point and thermal stability.

Ti_2AlC was first synthesized and its structure was elucidated in the early 1960s [2]. In recent decades, various processes were employed to synthesize bulk Ti_2AlC samples, however, it is very difficult to fabricate phase-pure Ti_2AlC. More recently, Barsoum *et al*. [3, 4] successfully fabricated high-purity Ti_2AlC polycrystal by reactively hot-pressing and high isostatic pressing (HIP) a mixture of Ti, graphite and Al_4C_3 powders. Wang *et al*. [5] also synthesized polycrystalline Ti_2AlC by using a solid-liquid reaction and simultaneous densification method. However, these processes are very complex. Thus further work is needed to develop new methods for the synthesis of Ti_2AlC. In the present research, spark plasma sintering of the elemental powders is reported. Elemental powders of Ti (99.0% pure, 10.6 μm), Al (99.8% pure, 12.8 μm) and carbon black (99%, 13.2 μm) (all from the Institute of Non-Ferrous Metals, Beijing, China) were used to synthesize Ti_2AlC. The mixture was first mixed leave ethanol for 24 h. Then it was filled into graphite crucibles, pre-pressed at 20 MPa, and sintered in vacuum (0.5 Pa) in the temperature range 1100 °C–1300 °C for 8 min by using a spark plasma sintering system (Mode SPS-1050, Lzumi Technology Co. Ltd). The heating rate was controlled at 80 °C/min and the applied pressure was maintained at a constant 30 MPa during reaction sintering. The synthesized samples were 20 mm in diameter and 4–6 mm in thickness. The sintered product was characterized by X-ray diffraction (XRD) using a rotating anode X-ray diffractometer (Model D/MAX-RB, Rigaku Corporation, Japan). The microstructures of the samples were investigated via scanning electron micrographs (SEM) (Model JSM-5610LV, Jeol Ltd., Japan), coupled with energy-dispersive spectroscopy (EDS) for chemical analysis (Model Phoenix, EDAX, USA).

It has been reported [6, 7] that the purity of Ti_3SiC_2 synthesized from Ti/Si/C powders is very sensitive to departures from the stoichiometric composition. Like Si, Al evaporates easily when heated at high temperature. So a deficiency in Al favors the formation of TiC. In the present research, samples with three different starting molar ratios (a) Ti:Al:C = 2:1:1; (b) Ti:Al:C = 2:1.1:1; (c) Ti:Al:C = 2:1.2:1 were investigated.

Fig. 1 shows the X-ray diffraction patterns of resultant products. The main phase in sample (a) was Ti_2AlC, but it contained quite a large amount of TiC. No second phase was identified by X-ray diffraction in samples (b) and (c). This indicates that their products were pure Ti_2AlC. In sample (c), the X-ray diffraction peaks of Ti_2AlC were much stronger than those of sample (b). The results confirmed the expectation that the excess of Al would favor the synthesis of Ti_2AlC. Therefore, the composition of sample (c) was chosen for use in the following experiments.

Fig. 2 shows the X-ray diffraction patterns of the resultant products sintered at different temperatures from 1100 °C to 1300 °C. At 1100 °C, no phase but Ti_2AlC was identified by X-ray diffraction, which indicated that the products were of high-purity Ti_2AlC. For the sample sintered at 1200 °C, the peak of Ti_2AlC became weaker and a very strong peak of TiC was identified by X-ray diffraction. When the sintering temperature reached 1300 °C, TiC was also present, but the peaks were weaker than at 1200 °C and the X-ray diffraction peaks of Ti_2AlC almost disappeared at the same time. The main phase was Ti_3AlC_2, which indicated that at 1300 °C, Ti_2AlC reacted with TiC to form Ti_3AlC_2. This result is consistent with previous work [5].

The measured lattice parameters of Ti_2AlC were $a = 0.3058$ nm, $c = 1.3649$ nm; these are very close to these reported by other authors [4, 5]. The measured density of bulk material sintered at 1100 °C was 4.10 g/cm^3, which is 99.8% of the theoretical density of Ti_2AlC. It can be concluded that high purity Ti_2AlC material can be synthesized by SPS from the starting powders mixtures with a molar ratio Ti:Al:C = 2:1.2:1.

Fig. 3 shows the scanning electron micrographs of the fracture faces of samples sintered at 1100 °C. In sample (a), two kinds of grains can be seen from the micrographs. Energy-dispersive spectroscopy (EDS) analysis revealed that the smaller grains in flocculent form were TiC. The larger laminated grains were Ti_2AlC. In sample (b) the Ti_2AlC was tabular, which is quite analogous to the crystalline shape of Ti_3SiC_2. The average diameter of the grains was about 20 μm, and there were about 5 μm in thickness. The layered nature of the Ti_2AlC grains is clearly seen in the fracture surface. No

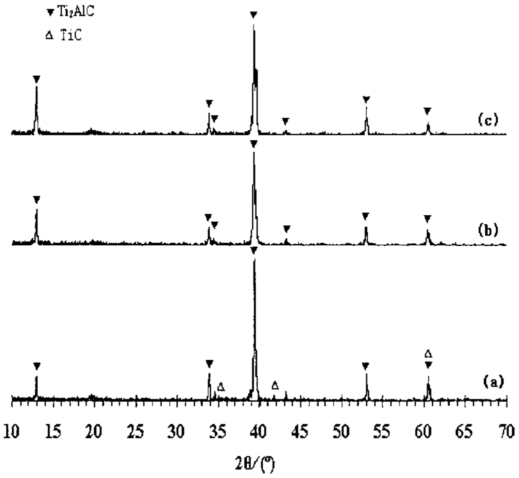

Figure 1 XRD patterns of sample (a) with the starting composition of Ti_2Al_1C; (b) with the starting composition of $Ti_2Al_{1.1}C$; and (c) with the starting composition of $Ti_2Al_{1.2}C$.

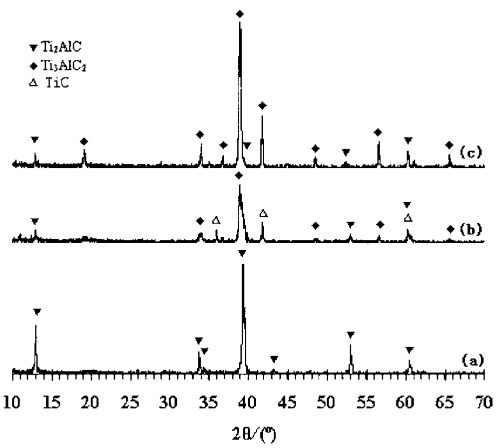

Figure 2 XRD patterns of samples sintered at different temperatures (a) 1100 °C; (b) 1200 °C; and (c) 1300 °C.

other phases appeared. These results also show that a deficiency in Al usually favors the formation of TiC.

More importantly, the material had the same machinability as graphite. It could easily be machined with ordinary mechanical machining tools, and holes could readily be drilled by using common steel drills without adding lubrication.

It is concluded that high-purity polycrystalline bulk Ti_2AlC was synthesized by spark plasma sintering of an elemental powder mixture with a molar ratio of Ti:Al:C = 2:1.2:1. The ideal synthesis temperature was

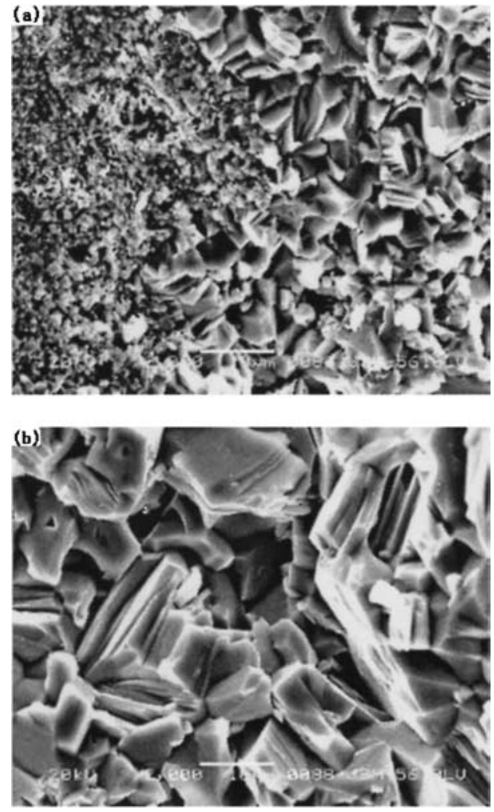

Figure 3 SEM photographs of the fracture faces of Ti_2AlC material synthesized from different starting compositions: (a) Ti_2Al_1C and (b) $Ti_2Al_{1.2}C$.

1100 °C, which is the lowest temperature for fabricating high-purity Ti_2AlC material reported so far.

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Received 14 March
and accepted 10 September 2003