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Synthesis of high-purity bulk Ti_2AlN by spark plasma sintering (SPS)

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Abstract

Single-phase bulk Ti_2AlN was prepared by spark plasma sintering (SPS) at 1200 °C of Ti/Al/TiN powders in stoichiometric proportion. Investigated by X-ray diffraction (XRD) of samples and the sintering process parameter, the reaction procedure could be analyzed. Scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) coupled with energy-dispersive spectroscopy (EDS) were utilized to investigate the morphology characteristics. When sintered at 1200 °C, Ti_2AlN phase was well developed with a close and lamellated structure. The distribution of Ti_2AlN grains was homogeneous.
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Keywords: A. Sintering; A. Pressing; B. X-ray methods; Microstructure

1. Introduction

Ti_2AlN belongs to the ternary compounds class with the general formula $M_{n+1}AX_n$ (n = 1–3). It possesses metal-like properties including electrical conductivity, thermal conductivity, and easy machinability, while demonstrating oxidation resistance, refractory behavior, and insusceptibility to thermal shock, typical of ceramics. Like Ti_3SiC_2 and Ti_2AlC, Ti_2AlN was found to be relatively soft (3–6 GPa) and readily machinable [1]. These unusual sets of properties make it candidate for many high temperature applications.

Recently, the research interest is Ti_2AlN thin films [2,3]. The fabrication of single phase, bulk dense samples of Ti_2AlN, has been proved to be very difficult. Barsoum et al. have fabricated Ti_2AlN by hot isostatically pressing (HIP) at 1600 °C for 4 h or 1400 °C for 48 h a mixture of Ti and AlN powders, but containing anywhere between 10 and 15 vol% of ancillary phases [1,4]. Recently, Jordan and Thadhani revealed that Ti_2AlN material could be fabricated by shock densification and subsequent reaction synthesis of Ti and AlN powders which were pressed and shock compressed at calculated peak pressures of 5 and 9 GPa, but TiN was present in addition to Ti_2AlN [5]. So far, no relevant synthesis report about bulk Ti_2AlN has been found.

2. Experimental procedures

All of the work was conducted using powder mixtures of TiN (99.3% pure, 2.03 μm), Ti (99.0% pure, 2.48 μm) and Al (99.8% pure, 1.50 μm) (all from Institute of Non-Ferrous Metals, Beijing, China). In brief, the mixture with a designed composition of Ti:Al:TiN = 1:1:1 was firstly mixed in ethanol for 24 h and dried at 60 °C for 2 h, then was filled into a graphite dies of Ø 16 mm in diameter, and finally sintered in spark plasma sintering (SPS) (Dr SINRER1020, IZUMI Technology Co. Ltd.). The samples were heated at a rate of 80 °C/min, in a Vacuum of 0.4 Pa; the soaking time was 10 min, and the pressure was 30 MPa.

The sintered product was characterized by X-ray diffraction (XRD) using a rotating anode X-ray diffraction (D/MAX-RB). The microstructures of the samples were investigated via scanning electron micrographs (SEM, JSM-5610LV) and electron probe micro-analysis (EPMA, JXA-8800R) coupled with energy-dispersive spectrum (EDS, Model Phoenix).

3. Results and discussion

3.1. XRD patterns of samples

Fig. 1 is the X-ray diffraction patterns of samples obtained from the mixture of raw materials ingredients of Ti + Al + TiN (in mole) sintered at the temperature range of 1000–1200 °C.

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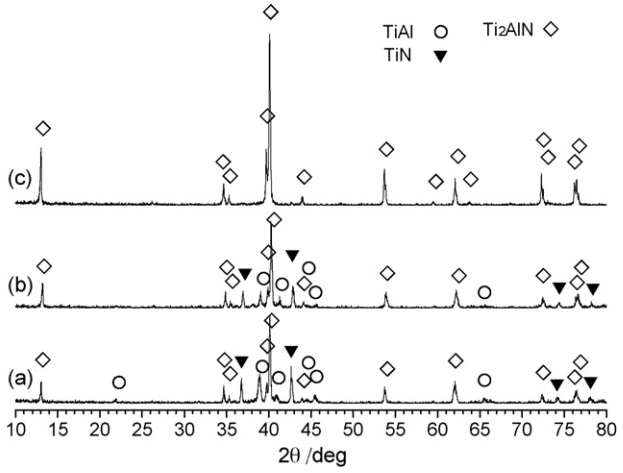

Fig. 1. XRD patterns of samples sintered at: (a) 1000 °C, (b) 1100 °C, and (c) 1200 °C.

Sintered at 1000 °C shown in Fig. 1(a), the main phases were Ti_2AlN, TiAl and TiN. When sintering temperature reached 1100 °C shown in Fig. 1(b), it was evident that the content of TiN and TiAl reduced and the peak value of Ti_2AlC intensified gradually. It was considered following reaction occurred: TiAl + TiN → Ti_2AlN. For samples sintered at 1200 °C, the products were of pure Ti_2AlN, no phase but Ti_2AlN was identified by X-ray diffraction. The diffraction peak of Ti_2AlN showed sharpest at 1200 °C, so the crystal of Ti_2AlN developed gradually by the rising temperature and the best crystallinity of Ti_2AlN was at 1200 °C.

3.2. The process parameters in spark plasma sintering course

Further insight could be gained by analyzing the temperature dependence of the vacuum pressure in the chamber, as shown in Fig. 2(a). The vacuum pressure reached a peak during the temperature of 800–1100 °C, which is a intensive reaction course. Pa values of samples remained constant beyond this temperature range. Fig. 2(b) shows the temperature dependence of *Z*-axis displacement. It could be seen that the sample densified rapidly during the temperature of 500–600 °C and 900–1100 °C. The *Z*-axis displacement was 1.09 mm.

Table 1
Atomic ratios of Ti, Al and N in the microscope of samples

at.%	Ti	Al	N	n(Ti):n(Al):n(N)
1	49.41	21.11	29.48	$Ti_2Al_{0.85}N_{1.19}$
2	50.28	20.95	28.77	$Ti_2Al_{0.83}N_{1.14}$
3	51.51	21.17	27.32	$Ti_2Al_{0.82}N_{1.06}$
The whole	50.40	21.08	28.52	$Ti_2Al_{0.83}N_{1.13}$

In the spark plasma sintering process, the gas in the chamber is discharged out at a constant rate. As a result, the vacuum pressure does not change during the ordinary sintering process. However, the pressure may appear as a peak once a large quantity of gas is produced from a reaction in the sample. Investigated by the process parameters in spark plasma sintering course, the phase formation and densification of Ti_2AlN is a intensive process during the temperature of 800–1100 °C.

3.3. Microstructure of Ti_2AlN samples

Fig. 3(a and b) are second electron images (SEI) of the fracture surfaces sintered at 1100 and 1200 °C by scanning electron micrographs. Ti_2AlN was underdeveloped sintered at 1100 °C with a loosen structure. When sintered at 1200 °C, Ti_2AlN phase was well developed with a close and lamellated structure. The grains were plate-like having the sizes of 8–12 and 20–30 μm, in thickness and elongated dimension, respectively. Fig. 3(c) shows a backscattered electron image (BEI) of the polished surfaces by electron probe micro-analysis. Three microzones with different contrast were selected, corresponding with energy-dispersive spectra shown in Fig. 3(d). The chemical analysis results listed in Table 1 revealed that the atomic ratio of Ti to Al in the sintered product (=2.41) is larger than that in the starting mixture (=2). As we know, the saturated vapor tension of Al at a high temperature is larger than that of Ti at the same temperature. When a sample is heated at a high temperature, the loss rate of Al by evaporation must be larger than that of Ti. The atomic ratio of Ti, Al and N is nearly to the stoichiometric proportion 2:1:1.

Fig. 4 shows the backscattered image of Ti_2AlN samples sintered at 1200 °C. The scan line of Ti element and Al element

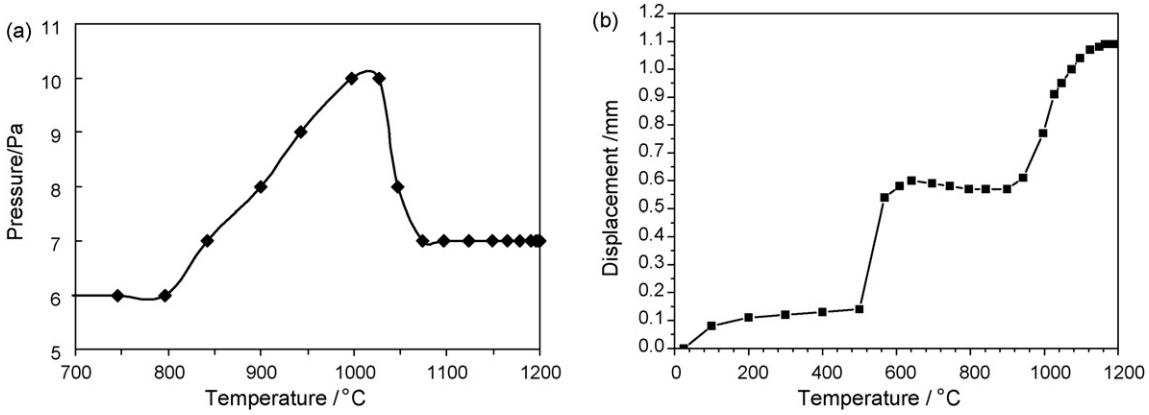

Fig. 2. The temperature dependence of: (a) vacuum, (b) *Z*-axis displacement.

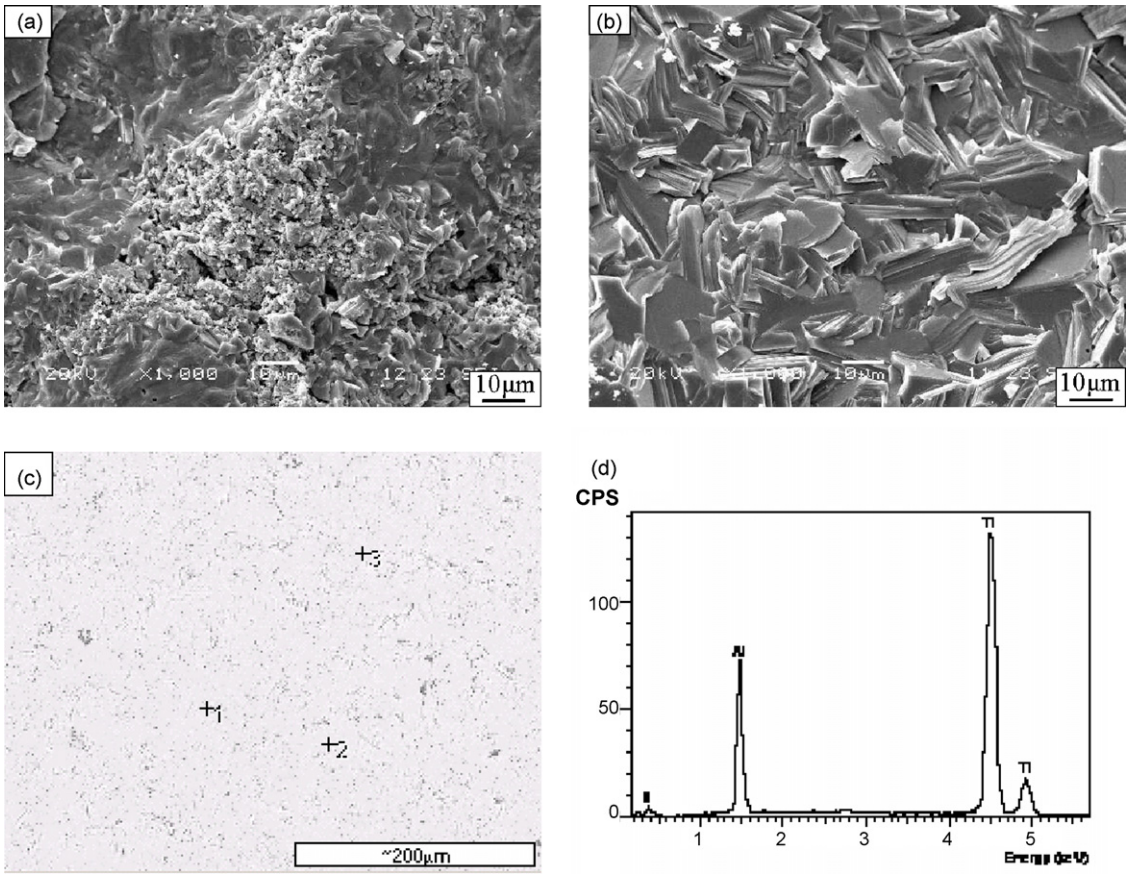

Fig. 3. Images of the Ti_2AlN samples: (a) SEI of the fracture surfaces sintered at 1100 °C by SEM, (b) SEI of the fracture surfaces sintered at 1200 °C by SEM, (c) BEI of the polished surfaces by EPMA sintered at 1200 °C, (d) energy-dispersive spectra of microzone.

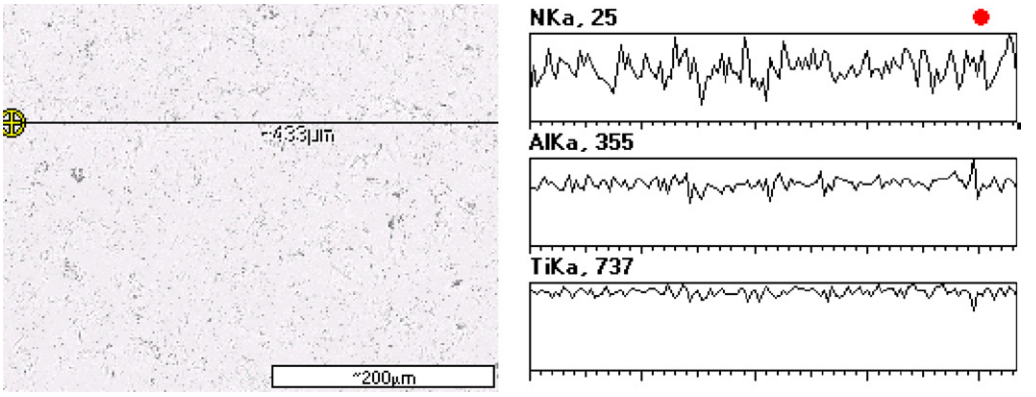

Fig. 4. EPMA backscattered image and elemental line scan image of Ti_2AlN samples sintered at 1200 °C.

shows constant. The scan line of N element fluctuates unsteadily, because EPMA was not suitable for determining ultra-light elements such as C and N. From the image of elemental line scan, the distribution of Ti_2AlN grains was homogeneous.

4. Conclusions

It is concluded that high-purity bulk Ti_2AlN materials and density could be synthesis by spark plasma sintering the mixtures with the raw materials ingredients of Ti + Al + TiN (in molars). When sintered at 1200 °C, Ti_2AlN phase was well developed with a close and lamellated structure. The distribution of Ti_2AlN grains was homogeneous.

Acknowledgments

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