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Synthesis of high-purity Ti_2AlN ceramic by hot pressing

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Abstract: High-purity Ti_2AlN ceramic was prepared at 1300 ℃ by hot pressing(HP) of Ti/Al/TiN powders in stoichiometric proportion. The sintered product was characterized using X-ray diffraction(XRD) and MDI Jade 5.0 software (Materials Data Inc, Liverpool, CA). Scanning electron microscopy(SEM) and electron probe micro-analysis(EPMA) coupled with energy-dispersive spectroscopy(EDS) were utilized to investigate the morphology characteristics. The results show that Ti_2AlN phase is well-developed with a close and lamellar structure. The grains are plate-like with the size of 3−5 μm, thickness of 8−10 μm and elongated dimension. The density of Ti_2AlN is measured to be 4.22 g/cm^3, which reaches 97.9% of its theory value. The distribution of Ti_2AlN grains is homogeneous.

Key words: Ti_2AlN; synthesis method; microstructure; hot pressing; sintering

1 Introduction

Ti_2AlN belongs to the ternary compounds with the general formula of $M_{n+1}AX_n$ (n=1−3)[1−5]. It possesses metal-like properties including certain electrical conductivity, thermal conductivity, and easy machinability, while oxidation resistance, refractory behavior, and insusceptibility to thermal shock demonstrate its typical characteristics of ceramics. Like Ti_3SiC_2 and Ti_2AlC, Ti_2AlN has found to be soft (3 to 6 GPa) and readily machinable[6−9]. These unusual properties make it a candidate for many high temperature applications.

Recently, the researches have mainly been concentrated on Ti_2AlN thin films[10−13]. However, the fabrication of single phase, dense bulk samples of Ti_2AlN, has still remained difficult. BARSOUM et al[1] and MICHEL[14] have fabricated Ti_2AlN by hot isostatically pressing(HIP) a mixture of Ti and AlN powders at 1 600 ℃ for 4 h or 1 400 ℃ for 48 h, but the product contained 10%−15% (volume fraction) ancillary phases, and the average grain size was 100 μm. JORDAN et al[15] revealed that Ti_2AlN material could be fabricated by shock densification and subsequent reaction synthesis of Ti and AlN powders, in which pressing and shock compression were performed at calculated peak pressures of 5 and 9 GPa, but TiN was present in addition to Ti_2AlN. So far, no other relevant synthesis report about bulk Ti_2AlN has been found. The objective of this work was to fabricate bulk Ti_2AlN with high-purity by hot pressing(HP). And the microstructure was especially investigated.

2 Experimental

The powder mixture of TiN (99.3% purity, 2.03 μm), Ti (99.0% purity, 2.48 μm) and Al (99.8% purity, 1.50 μm) (all from Institute of Non-Ferrous Metals, Beijing, China) as used with a designed composition of Ti:Al:TiN=1:1:1 in molar ratio. The mixture was firstly mixed in ethanol for 24 h, and then was sintered by HP. In the HP processing, the samples were heated in Ar at a rate of 50 ℃/min until the requisite temperature was reached, and kept for 2 h. The preparing pressure was 30 MPa.

The sintered product was characterized by X-ray diffraction (XRD, D/MAX-RB) and MDI Jade 5.0 software (Materials Data Inc, Liverpool, CA). The microstructures of the samples were investigated via scanning electron micrographs (SEM, JSM-5610LV) and

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electron probe micro-analysis (EPMA, JXA-8800R) coupled with energy-dispersive spectrum (EDS, Model Phoenix). The density of the sintered product was measured by Archimedes method.

3 Results and discussion

3.1 XRD patterns

Fig.1 shows the X-ray diffraction patterns of samples obtained from the mixture of raw materials of Ti+Al+TiN sintered at the temperature range of 1 200−1 400 ℃. When being sintered at 1 200 ℃ shown in Fig.1(a), the main phases are Ti_2AlN, TiAl and TiN. For samples sintered at 1 300 ℃, the products are composed of pure Ti_2AlN, and the diffraction peak of TiAl and TiN disappears. It is considered that the following reaction occurs: TiAl+TiN → Ti_2AlN. The diffraction peak of Ti_2AlN shows the sharpest peak at 1 300 ℃, so the crystal of Ti_2AlN is developed gradually by rising the temperature and the best crystallinity of Ti_2AlN is got at 1 300 ℃. When the sintering temperature reaches 1 400 ℃, as shown in Fig.1(c), Ti_2AlN is decomposed into Ti_4AlN_3 and $TiAl_3$. The mechanics of this process needs to be studied in more details.

Fig.2 shows the X-ray diffraction patterns analyzed by MDI Jade 5.0 software, which can perform powder diffraction data analysis and acquisition. No phase but Ti_2AlN is identified when the sintering temperature reaches 1 300 ℃. The indices of crystallographic plane are marked. The sintering product Ti_2AlN has higher purity than others, owning to the high activity of element Al in raw materials.

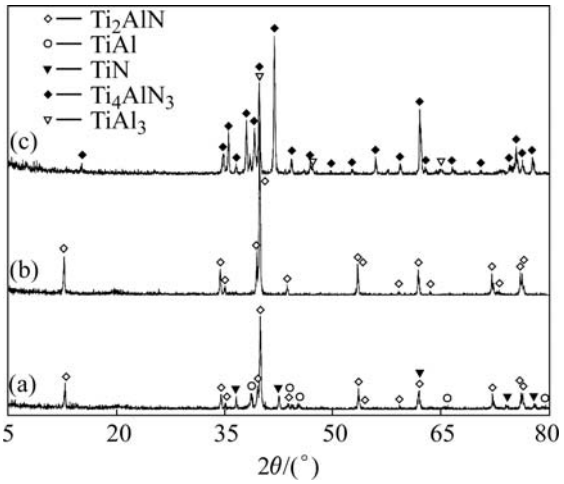

Fig.1 XRD patters of samples sintered at 1 200 ℃ (a), 1 300 ℃ (b) and 1 400 ℃ (c)

3.2 Microstructure

Figs.3(a) and (b) show the second electron images (SEI) of the fracture surfaces sintered at 1 200 ℃ and 1 300 ℃. Ti_2AlN is underdeveloped when being sintered at 1 200 ℃ with a loosen structure. When being sintered at 1 300 ℃, Ti_2AlN phase is well-developed with a close and lamellar structure. The grains are plate-like with the size of 3−5 μm, thickness of 8−10 μm and elongated dimension. The grain size is much smaller than that by HIP[1,14], because the sintering temperature is lower and time is less by HP than those by HIP. Fig.3(c) shows a backscattered electron image(BEI) of the polished surfaces by electron probe micro-analysis (EPMA). Three microzones with different contrast are selected, corresponding with energy-dispersive spectra

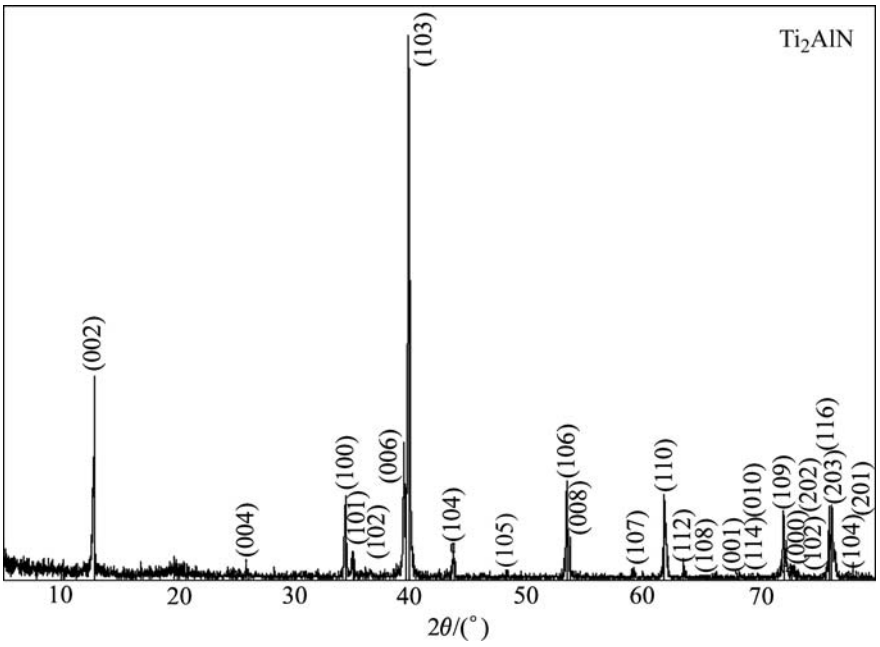

Fig.2 X-ray diffraction patterns of samples sintered at 1 300 ℃ analyzed by MDI Jade 5.0 software

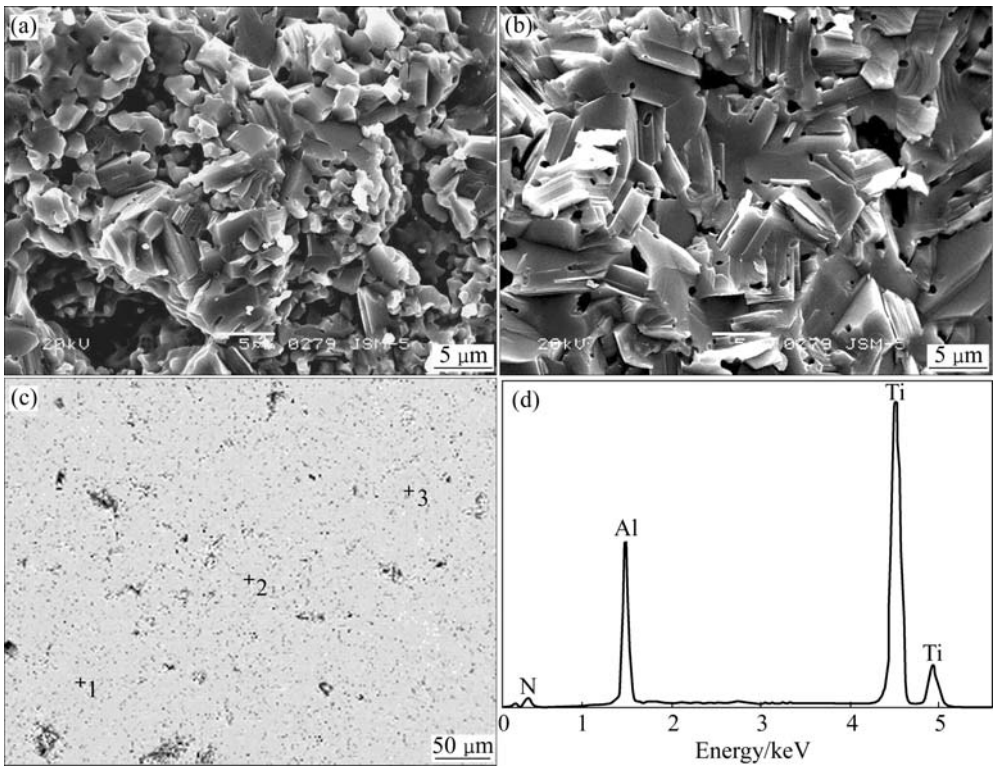

Fig.3 Images of Ti_2AlN samples: (a) SEI of fracture surfaces sintered at 1 200 ℃ by SEM; (b) SEI of fracture surfaces sintered at 1 300 ℃ by SEM; (c) BEI of polished surfaces by EPMA sintered at 1 300 ℃; (d) Energy-dispersive spectra of microzone

(EDS), as shown in Fig.3(d). The chemical analysis results listed in Table 1 reveal that the molar ratio of Ti to Al in the sintered product (2.25) is larger than that in the starting mixture (2). As we know, the saturated vapor tension of Al at high temperature is larger than that of Ti at the same temperature. When the sample is heated at a high temperature, the loss rate of Al by evaporation must be larger than that of Ti. The molar ratio of Ti, Al and N is nearly to the stoichiometric proportion of 2:1:1. The density of Ti_2AlN prepared at the optimal synthetic temperature of 1 300 ℃ is 4.22 g/cm^3, which reaches 97.9% of its theory value (4.31 g/cm^3).

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

Point	*x*/%			*n*(Ti):*n*(Al):*n*(N)
	Ti	Al	N	
1	51.42	22.10	26.47	2:0.86:1.03
2	49.54	24.34	26.12	2:0.98:1.05
3	50.71	21.25	28.04	2:0.84:1.11
Average	50.56	22.56	26.88	2:0.89:1.06

Fig.4 shows the back scattered image of Ti_2AlN samples sintered at 1 300 ℃. The scan lines of Ti element and Al element show constant. The scan line of N element fluctuates unsteadily, because EPMA is not suitable for determining ultra-light elements such as C

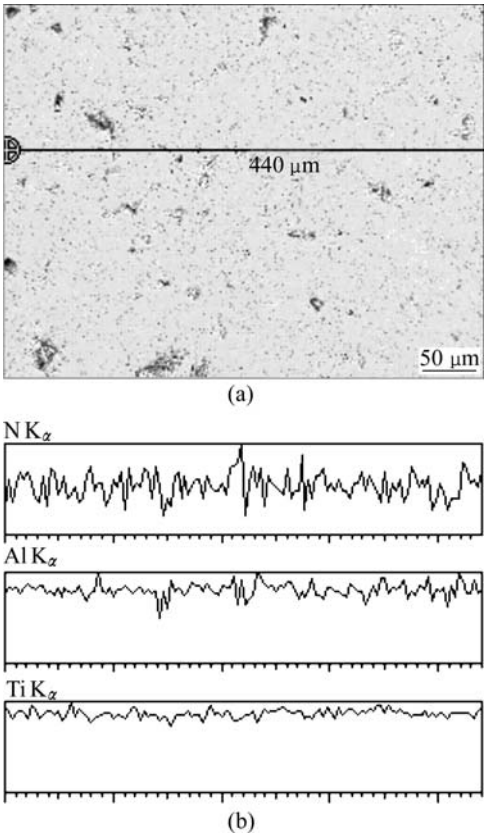

Fig.4 EPMA back scattered image (a) and elemental line scan (b) of Ti_2AlN samples sintered at 1 300 ℃

and N. From the analysis of elemental line scan, the distribution of Ti_2AlN grains is homogeneous.

4 Conclusions

1) Bulk Ti_2AlN materials with high-purity can be fabricated by hot-pressing the mixtures of Ti+Al+TiN.

2) When being sintered at 1 300 ℃, Ti_2AlN phase is well-developed with a close and lamellar structure. The grains are plate-like with the size of 3−5 μm, thickness of 8−10 μm and elongated dimension.

3) The density of Ti_2AlN is 4.22 g/cm^3, which reaches 97.9% of its theory values, and the distribution of Ti_2AlN grains is homogeneous.

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