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ARTICLE

Reactive Synthesis of Polycrystalline Ti_3AlC_2 and Its Sintering Behavior

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Abstract: A method for fabrication of ternary compound Ti_3AlC_2 powder by pressureless calcining (PC) technique was developed. Powders of Ti, Al and TiC were mixed as staring materials. The effects of calcining temperature and aluminum content on the purity of Ti_3AlC_2 were discussed. The reaction mechanism and the microstructure evolution of Ti_3AlC_2 prepared at different temperatures were investigated by X-ray diffraction, field emission scanning electron microscopy and high resolution transmission electron microscopy. Results indicate that the single-phase polycrystalline Ti_3AlC_2 powders are obtained at 1300 ℃, which possesses a typical laminated structure, and the best molar ratio of raw Ti/Al/TiC materials is 1:1.2:2. The bulk samples sintered by hot pressing were from the Ti_3AlC_2 powders. After hot pressing of different temperatures, the fully dense bulk Ti_3AlC_2 shows the best properties when prepared at 1300 ℃. The density of bulk Ti_3AlC_2 reaches to 99.9%. The average Vickers hardness is around 5.7 GPa, and the maximum flexural strength is over 630 MPa. Finally the strengthening mechanism of the bulk Ti_3AlC_2 was also proposed.

Key words: Ti_3AlC_2; reaction mechanism; sintering behavior

Ti_3AlC_2 (titanium aluminum carbide) is a classic member of so-called “312” ternary carbides material with layered structure among the MAX phases, which has been attracting great attention since it possesses many unusual properties of both metals and ceramics[1]. Similar to Ti_3SiC_2, Ti_3AlC_2 is an excellent material with low density ($4.25g/cm^3$), low thermal expansion coefficient, high modulus, and high strength at high temperature, high temperature oxidation resistance, high thermal stability, high melting point and great irradiation tolerance[2-5]. In addition, Ti_3AlC_2 is thermally and electrically conductive, and being machinable with conventional tools without any lubrication[6-8]. Meanwhile, Ti_3AlC_2 exhibits some abnormal room-temperature compressive plasticity compared to the normal brittle ceramics[9]. Such a remarkable combination of properties suggests that it may be a promise material for many applications especially in the field of high temperature materials.

Accurately, the discovery of MAX phase dates back to early 1960s. However, due to the difficulty of synthesis, Ti_3AlC_2 was first synthesized by Pietzka and Schuster until 1994. After that, in order to meet the increasing demand of society, various methods were applied to fabricate high-purity polycrystalline Ti_3AlC_2, such as hot pressing (HP), hot isostatic pressing (HIP), combustion synthesis (SHS), spark plasma sintering (SPS) and slip casting (SC)[1].

However, all above methods mentioned need very rigorous production conditions, including high temperature, high pressure and long sintering time, which have a shortcoming of inefficiency. Thus, mass production from these methods is restricted. Fortunately, pressureless calcining (PC), a conventional powder metallurgy route, is pretty suitable to establish a process that can be used to mass-produce Ti_3AlC_2 with low cost and high-purity.

In the present paper, we adopted the pressureless calcining (PC) technique to synthesize Ti_3AlC_2 powder with

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high-purity. After hot pressing, fully dense Ti_3AlC_2 was successfully prepared. The microstructure and related mechanical properties were investigated, and the strengthening mechanism of bulk Ti_3AlC_2 was also discussed.

1 Experiment

The powders of Ti (<45 μm, 99.9%), Al (<75 μm, 99.5%) and TiC (<50 μm, 99%) were produced by General Research Institute for Nonferrous Metals Beijing, China in this experiment. The molar ratio of Ti:Al:TiC was 1:(1+x):2, (x=0.1, 0.2, 0.3), and slightly off-stoichiometric was selected for this study[10]. The powder mixtures were put in a stainless steel vacuum jar with alcohol. Subsequently, the mechanical milling process was conducted by ball mill with a rotation speed of 400 r/min, and the mass ratio of ball to powders was 15:1. After dried in vacuum, the blended powders were sieved with 100-mesh screen. Then the mixture powders were pressureless calcined (PC) in flowing argon atmosphere. The temperature was selected in a range of 1100～1500 ℃, the heating rate was 10 ℃/min, and the holding time was 30 min.

In order to study the sintering behavior of high-purity Ti_3AlC_2, a hot pressing (HP) method was adopted by calcining the powder in argon protection under a constant axial pressure of 25 MPa, the sintering temperature was selected in the range of 1000～1400 ℃, and the holding time was 30 min. The phase of the sintered powders and bulks was identified by X-Ray diffractometry (XRD) with Cu Kα radiation at 30 kV and 40 mA. The microstructure was observed by a field emission scanning electron microscopy (FE-SEM) equipped with an energy-dispersive spectroscopy (EDS) system (Hitachi SU8020). Furthermore, JEM-2100F high resolution transmission electron microscopy (TEM) was used to analyze the Ti_3AlC_2 powder prepared by pressureless calcining at 1300 ℃. The measurements of all the mechanical properties were performed at room temperature. The density of solid samples was measured by Archimedes' method. The electrical resistance was measured by a double bridge method. And the Vickers hardness test was performed on the fine polished surface by HXD-1000 tester (Shanghai second optical Ltd, China) at a load of 1 N with the dwell time of 15 s. The flexural strength of bulk Ti_3AlC_2 specimen with dimensions of 3 mm×8 mm×35 mm was determined by the three-point bending method. In order to analyze the strengthening mechanism of bulk Ti_3AlC_2, the fracture of solid samples after three-point tests was also examined by SEM.

2 Results and Discussion

2.1 Effect of temperature on the synthesis of Ti_3AlC_2

Fig.1 shows the XRD patterns of the samples calcined in the temperature range of 1100～1500 ℃ from the milled powders of Ti/1.2Al/2TiC. As shown in Fig.1, un-reacted TiC is the main crystalline phase when the temperature is below 1250 ℃, while Ti-Al and Ti_2AlC appear as a minor phase when the sample calcined at 1100 ℃ for 30 min. However, when the temperature reaches to 1250 ℃, Ti-Al and Ti_2AlC almost disappear, but the intensity of TiC is negligible all the time. The presence of TiC suggests that it is not consumed completely to form Ti_3AlC_2 or Ti_2AlC in the reaction process. As the temperature increases to 1300 ℃, the content of TiC becomes minimal, indicating that a single-phase Ti_3AlC_2 is almost obtained. With further increase in calcining temperature, the relative intensity of TiC increases gradually, indicating that Ti_3AlC_2 slightly decomposes to form TiC above the temperature of 1300 ℃[10]. Therefore, the content of TiC suddenly becomes high when the temperature is below 1250 ℃ or above 1350 ℃, which means the temperature between 1250 ℃ and 1350 ℃ can be considered as the most suitable temperature to synthesize highly purity Ti_3AlC_2 powder. Obviously, it is clear that the purist Ti_3AlC_2 could be obtained at 1300 ℃, from the mixture powders of Ti/1.2Al/2TiC.

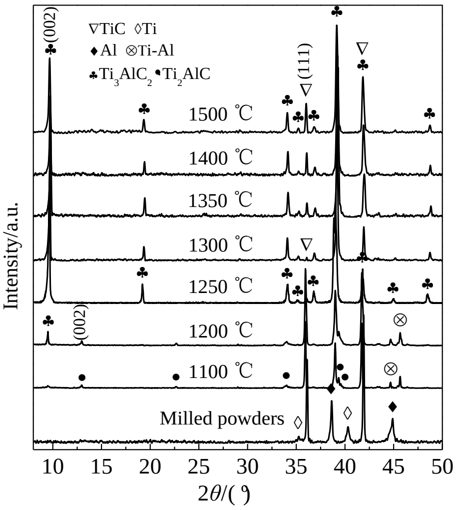

Fig.1 XRD patterns of milled powders and the samples calcined at 1100～1500 ℃ for 30 min

The reaction mechanism for synthesis of Ti_3AlC_2 from Ti/Al/TiC was discussed by previous study. The whole reaction process of synthesizing could be divided into three stages: preheating stage, initial reacting stage, dissolution and precipitation reacting stage[11]. The possible reactions can be expressed as follows[12-14]:

$$\mathrm{4Ti+2Al=Ti_3Al+TiAl} \tag{1}$$

$$\mathrm{Ti_3Al+2Al=3TiAl} \tag{2}$$

$$\mathrm{TiAl+TiC=Ti_2AlC} \tag{3}$$

$$Ti_2AlC+TiC=Ti_3AlC_2 \quad (4)$$

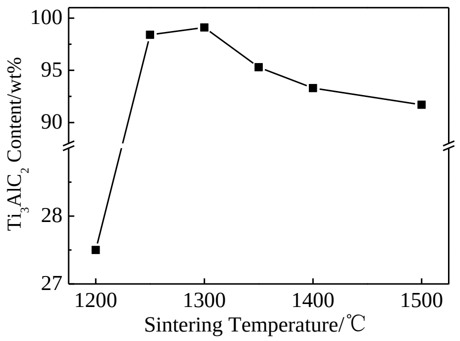

Fig.2 Ti_3AlC_2 content in Ti/1.2Al/2TiC samples as a function of temperature

In order to calculate the weight percent of the constituent phases of Ti_3AlC_2, Ti_2AlC and TiC in the synthesized product, the following equation were adopted[15]:

$$W_a = I_a / (I_a + 0.220 I_b + 0.084 I_c) \quad (5)$$

$$W_b = I_b / (4.545 I_a + I_b + 0.382 I_c) \quad (6)$$

$$W_c = I_c / (11.905 I_a + 2.619 I_b + I_c) \quad (7)$$

wherein, W_a, W_b and W_c represent the mass percentage of Ti_3AlC_2, Ti_2AlC and TiC, respectively. I_a, I_b and I_c are the integrated diffraction intensity of Ti_3AlC_2 (002) peak ($2\theta=9.5°$), Ti_2AlC (002) peak ($2\theta=13.0°$) and TiC (111) peak ($2\theta=35.9°$), respectively.

Fig.2 shows the purity of Ti_3AlC_2 in the synthesized samples calcined at 1200～1500 ℃. It can be seen that the content of Ti_3AlC_2 increases abruptly with the calcining temperature above 1200 ℃, and it becomes steady at around 1250 ℃. The highest purity of Ti_3AlC_2 could be obtained at 1300 ℃ with the value of about 98.4%. However, as the temperature continues to rise, the purity of Ti_3AlC_2 gradually declines, which means the Ti_3AlC_2 is mainly synthesized at 1200～1300 ℃. At high temperature, the purity of Ti_3AlC_2 is undesirable, mainly because of the excessive loss of un-reacted aluminum, and the decomposition of Ti_3AlC_2.

Fig.3a and 3b show the SEM microstructures of the samples calcined from Ti/1.2Al/2TiC powders at 1300 and 1400 ℃ for 30 min. The typical lamellar internal microstructure of polycrystalline Ti_3AlC_2 is observed at 1300 and 1400 ℃, which shows uniform, straight morphology and clear boundary. In Fig.3a and 3b, region B and D are enlarged micrographs of region A and C, respectively. The laminate thickness of Ti_3AlC_2 increases from 30 nm to 40 nm with the increase of temperature. Besides, the region D exhibits several layers of laminate which are combined to form a thick one; it is considered to be a growing mechanism of plate-like Ti_3AlC_2 at high temperature.

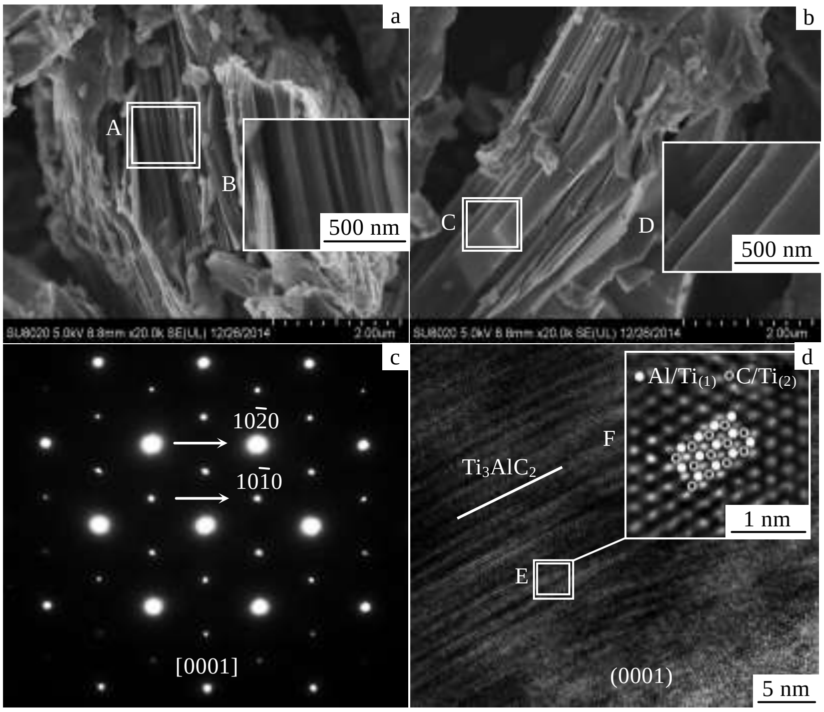

Fig.3 SEM images of the samples calcined from Ti/1.2Al/2TiC powders at different temperatures for 30 min: (a) 1300 ℃ and (b) 1400 ℃; (c) SAED pattern of Ti_3AlC_2 fabricated by PC technique at 1300 ℃; (d) HRTEM image of Ti_3AlC_2 grain, the region F is an en-

larged Fast Fourier transformation filtered image of the region marked E in Fig.3d

Fig.3c shows SAED pattern of hexagonal Ti_3AlC_2 indexed as [0001] for the sample of Ti_3AlC_2 powder synthesized at 1300 ℃. Fig.3d is an HR TEM image that shows the typical layered microstructure of a grain, and the basal (0001) plane is indicated. The region F is an enlarged Fast Fourier transformation filtered image of the region marked E in Fig.3d. The region F in Fig.3d shows a schematic arrangement of Ti_3AlC_2 in the (0001) plane. Ti_3AlC_2 crystallizes in $P6_3/mmc$ symmetry with two $Ti_{(1)}$ atoms at 2a, four $Ti_{(2)}$ atoms at 4f, two Al atoms at 2b and four C atoms at 4f position[16]. It can be described as two edge-sharing TiC_6 octahedral layers separated by two-dimensional close-packed aluminum layers[17]. Thus, the basal (0001) plane of Ti_3AlC_2 could not show three kinds of atoms in the same plane. As shown by schematic arrangement of Ti_3AlC_2 in region F, along the direction of [0001], it can be inferred that $Ti_{(1)}$ at 2a position overlap with Al atoms at 2b position, and $Ti_{(2)}$ atoms overlap with C atoms at 4f position.

2.2 Effect of Al content on the synthesis of Ti_3AlC_2

The evaporation of Al will occur at high temperature, and the deficiency of Al will change the proportion of mixtures in the reaction system, which suggests the slightly non-stoichiometric composition is necessary[12]. That's the reason why we choose the molar ratio of Ti/1.2Al/2TiC as the initial reactants.

Fig.4 shows the XRD patterns of resultant powders obtained by PC at 1300 ℃ for 30 min, with the original composition of Ti/(1+x)Al/2TiC (x=0.1, 0.2, 0.3). It can be seen that the impurity of TiC coexists with Ti_3AlC_2 all the time. when the content of Al reaches to 1.2, the intensity of TiC is lowest. However, when the Al content increases to 1.3, the excessive Al (x=0.3) reduces Ti_3AlC_2 purity with an increase of TiC peak. According to Eq.(7), when x=0.1, 0.2, 0.3, the TiC content is 3.5, 1.6, 3.2 wt%, respectively. This result reveals that the appropriate x should be determined as 0.2.

The off-stoichiometric of raw materials contributes to obtaining single-phase Ti_3AlC_2, but the reason is still not clear up to now. One possible reason is that the surplus Al is considered as a compensate for the loss[10,11]; the second explanation is that Al element provides a liquid circumstance to speed up the formation of Ti-Al and Ti_2AlC which are intermediate phases of Ti_3AlC_2[18].

2.3 Mechanical properties and fracture analysis of bulk Ti_3AlC_2

Fig.5 shows the variation of Vickers hardness and the relative density of Ti_3AlTi_2 sintered by hot pressing at 1000～1400 ℃ for 30 min under 25 MPa. The plastic deformation of Ti_3AlC_2 may occur when sintering temperature is above its brittle-ductile transition temperature (BBTT) in the range of 1000 to 1050 ℃[19,20], which contributes to improving the relative density and some other mechanical properties, such as Vickers hardness and flexural strength.

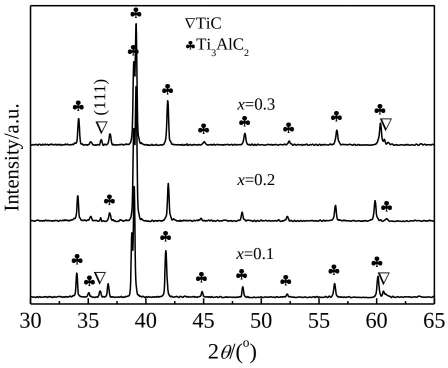

Fig.4 XRD patterns of Ti/(1+x)Al/2TiC samples calcined at 1300 ℃ for 30 min

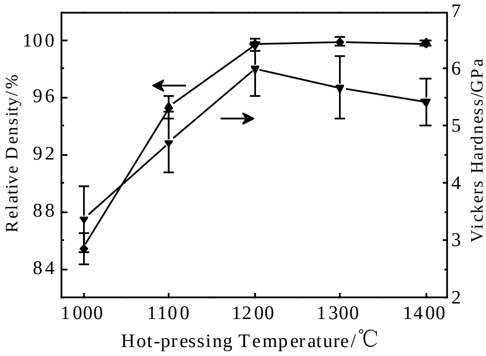

Fig.5 Variation of relative density and Vickers hardness of sintered Ti_3AlC_2 as a function of hot pressing temperature

It can be seen from Fig.5 that the relative density and Vickers hardness of the products increase gradually as functions of temperature. When the temperature is over 1200 ℃, the relative density maintains at more than 99.8%, and the Vickers hardness decreases instead. The high relative density of bulk samples are due to their special crystal properties and structure, which contribute to powder sintering. The Vickers hardness reaches about 5.7 GPa at 1200 ℃, and its increment between 1000~1200 ℃ may be ascribed to the increasing of the relative density. However, further increasing the sintering temperature, the Vickers hardness decreases due to the grain size coarsening. And Ti_3AlC_2 shows anisotropy in irregular deformations of the Vickers indentation, which disperses the hardness values due to the difficulty in precise measurement[16,20], and this is the reason for a relative lager deviation of the Vickers hardness value.

Fig.6 shows the variation of flexural strength and electrical conductivity of polycrystalline bulk of Ti_3AlC_2 as functions of hot pressing temperature. It can be seen that the electrical conductivity and flexural strength increase abruptly with the increasing of temperature from 1000 ℃ to 1200 ℃. This result is in good agreement with the increase of the relative density in Fig.5. Thus, the densification of Ti_3AlC_2 at those temperatures may be a main reason for this phenomenon. The electrical conductivity keeps the value around $2.8\times10^6\ \Omega^{-1}\ m^{-1}$ between 1200 ℃ and 1400 ℃, while the flexural strength decreases with hot pressing temperature increasing after it reaches a peak at 1300 ℃. The maximum flexural strength of Ti_3AlC_2 reaches to 630 MPa. In order to study the reinforcement mechanisms of bulk Ti_3AlC_2 with the sintering temperature above 1300 ℃, its thermal stability should be considered. There are essentially three types of chemical bonds in Ti_3AlC_2. The calculations show that $Ti_{(2)}$-Al bonds are the weakest and whereas the $Ti_{(2)}$-C bonds are the strongest[2], which results in the transformation of Ti_3AlC_2 into TiC_x and Al_2O_3 at high temperature. When the sintering temperature reaches to 1300 ℃, few un-reacted TiC and in situ formed Al_2O_3 particles could be detected by XRD in the Ti_3AlC_2 samples (not shown here for brevity)[21], even if that temperature is below the real decomposition temperature (1460 ℃) of pure Ti_3AlC_2[4]. Thus, the existence of a few un-reacted TiC and in situ formed Al_2O_3 may act as another important reason to increase the flexural strength of Ti_3AlC_2 effectively[22].

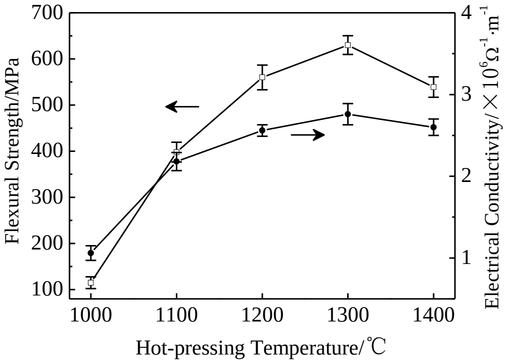

Fig.6 Flexural strength and electrical conductivity of sintered Ti_3AlC_2 as functions of hot-pressing temperature

In order to analyze the strengthening mechanism of bulk Ti_3AlC_2 sintered at 1300 and 1400 ℃, the fractures of bulk Ti_3AlC_2 are obtained by SEM. Fig.7b and 7d are the enlarged micrographs of Fig.7a and 7c, respectively. The traces of delamination, buckling and sliding of the grains are obvious, and some lamellas are broken and pulled out, leaving many long dents denoted by arrows in Fig.7b and 7d. Those features can exhaust much energy and give Ti_3AlC_2 a damage-tolerance capability[20]. When the basal planes of Ti_3AlC_2 are parallel to the crack propagation, the grain delamination occurs. When the basal planes are normal to the crack propagation, the nano-sized layers and the cracking of the grain boundaries (region A in Fig.7d) also absorb a lot of energy, resulting in many laminated layers[21]. It can be seen that the intergranular fracture and transgranular fracture coexist in the bulk Ti_3AlC_2 prepared at two different temperatures. The sample of Ti_3AlC_2 prepared at 1300 ℃ exhibits the apparent intergranular fracture mode in Fig.7a. However, Fig.7c shows typical laminated layers and flat features, which means transgranular fracture is dominant in the bulk Ti_3AlC_2 prepared at 1400 ℃. The laminates arrangements represent grains with clear different

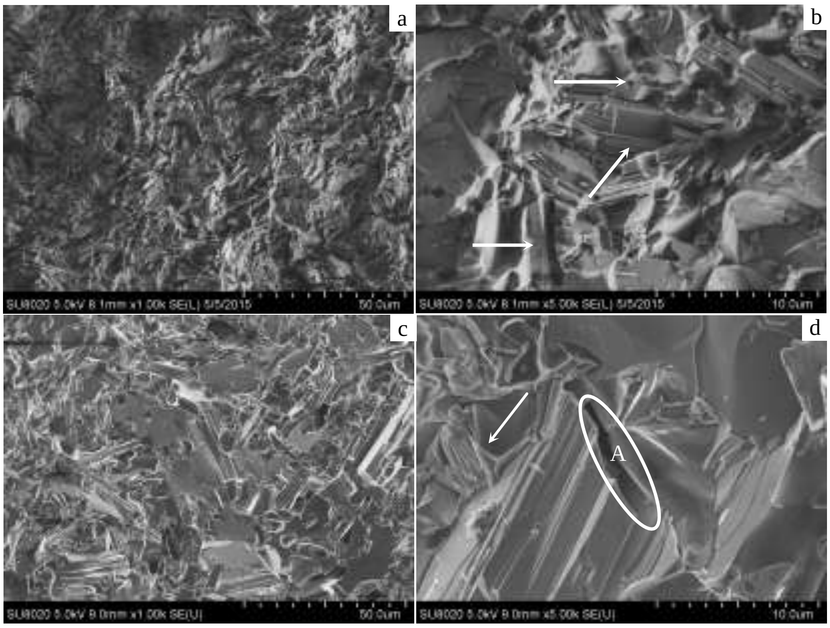

Fig.7 SEM images of typical fracture surface in the Ti_3AlC_2 sample prepared at 1300 ℃ (a, b) and 1400 ℃ (c, d) for 30 min under 25 MPa

orientations in Fig.7c. It is obvious that the Ti_3AlC_2 grains are elongated[23]. With the grain growth, the grain may be more prone to breakage, and the intergranular fracture hardly occurs at this temperature due to the special elongated grain structure. That's the reason why transgranular fracture is weaker than the intergranular in bulk Ti_3AlC_2. Thus, the grains growth and their elongated grain structures are considered to be the two possible reasons for the decline of the flexural strength.

3 Conclusions

1) High-purity Ti_3AlC_2 has been fabricated successfully from Ti/1.2Al/2TiC powder mixtures by pressureless calcining at 1300 ℃. The excess content of Al in the starting materials can effectively improve the purity of Ti_3AlC_2 powder.

2) Fully dense bulk Ti_3AlC_2 is successfully fabricated by hot pressing from pure Ti_3AlC_2 powder at 1200～1400 ℃. The typical laminated structure of ternary carbides is observed in both powder and bulk of Ti_3AlC_2. Besides, the thickness of laminates can be adjustable depending on calcining or sintering temperature.

3) The better properties of bulk Ti_3AlC_2 are obtained at 1300 ℃ with the average relative density, Vickers hardness, electrical conductivity and three-point bending strength of the samples being (99.9±0.3)%, (5.7±0.5) GPa, $(2.8\pm0.1)\times10^6\ \Omega^{-1}\cdot m^{-1}$ and (630±20) MPa, respectively.

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Ti_3AlC_2材料的反应合成及其烧结行为

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摘 要：以Ti，Al和TiC为原材料，用无压煅烧合成法制备三元化合物Ti_3AlC_2。详细讨论了煅烧温度和铝含量对多晶Ti_3AlC_2纯度的影响。利用X射线衍射仪、场发射扫描电镜和场发射透射电镜研究了粉末材料的组织结构、晶粒大小、层板厚度和选区电子衍射花样。结果表明1300 ℃是合成Ti_3AlC_2粉末的最佳煅烧温度，1:1.2:2是Ti/Al/TiC原材料的最佳摩尔比。用热压法制备了不同烧结温度下的Ti_3AlC_2块体试样，在1300 ℃热压制备的Ti_3AlC_2块体的相对密度可达99.9%，其维氏硬度和三点抗弯强度分别为5.7 GPa和630 MPa。通过场发射扫描电镜观察材料的断口形貌，进一步分析了Ti_3AlC_2块体材料的强化机理。

关键词：Ti_3AlC_2；反应机理；烧结行为

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