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Fabrication of Ti_2AlC by hot pressing of Ti, TiC, Al and active carbon powder mixtures

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Polycrystalline Ti_2AlC samples were synthesized by hot pressing of Ti, Al, TiC and active carbon powder mixtures. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used for phase identification and microstructure evaluation. No other phase except Ti_2AlC was detected in samples synthesized by hot pressing of the 0.5TiC/1.5Ti/1.0Al/0.5C powder mixtures at 1400°C for 1 and 3 h under a pressure of 30 MPa. The densities of these two samples were 96.1 and 98% of the theoretical value of pure Ti_2AlC, respectively. The reason that the densities of these two samples were lower than the theoretical density of pure Ti_2AlC is that pore existed in these two samples. At lower temperature of 1300°C, the speed of the reaction forming Ti_2AlC was slow. While at higher temperature of 1500°C, Ti_2AlC transformed to Ti_3AlC_2. So these two temperatures are not suitable for the fabrication of Ti_2AlC.

1. Introduction

Ternary carbide Ti_2AlC belongs to a special class of materials known as layered compounds or "machinable ceramics". It is hexagonal and has a unit cell with lattice parameters of $a = 0.304$ and $c = 1.360$ nm respectively. The theoretical density of Ti_2AlC is 4.11 g/cm^3. In the crystal structure of Ti_2AlC, Ti and C atoms form Ti—C transition metal octahedra. Every layer of Ti_6C octahedra is interleaved with a layer of pure Al atoms [1]. The Ti—C bonding is mainly covalent and ionic bond and is strong while the Ti—Al bonding is metallic bond and is relatively weak especially when shearing [2, 3]. Such layered structure endows Ti_2AlC an unusual set of properties: like metals, it is thermally and electrically conductive, easy to be machined with conventional tools without lubrication and resistant to thermal shock; like ceramics it presents a high strength, high melting point and thermal stability, has relatively low coefficients of thermal expansion, and combines mechanical anisotropy with thermal isotropy [4]. Such combination of excellent properties makes it a promising material for many kinds of applications.

It took hundreds of hours to fabricate Ti_2AlC powders for the first time [1]. Then progress was achieved and attention was focused on the fabrication of bulk Ti_2AlC material. Processes adopted generally include hot pressing and hot iso-static pressing. In the mid 1970s, Ivchenko *et al.* fabricated 90 to 92 pct dense compacts of Ti_2AlC and measured some of its properties [5, 6]. Bulk polycrystalline samples of Ti_2AlC with high purity and density were fabricated by reactively hot pressing (HP) or hot iso-static pressing (HIP) of Ti, Al_4C_3 and graphite powder mixtures [7, 8]. These two processes that Barsoum introduced require either high temperature (in hot pressing the temperature was as high as 1600°C) or long sintering time (in hot iso-static pressing the soaking time was 30 h) because the initial materials was Al_4C_3, which has a low reactivity.

Furthermore, the final product in these two processes contained about 4 vol% unwanted phase of Al_2O_3 because Al_4C_3 is hygroscopic and reacts with H_2O at room temperature and forms Al_2O_3. More recently, Wang *et al.* fabricated high purity dense Ti_2AlC by the solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process [9]. In this process elemental powder mixtures of titanium, aluminum and graphite were used as raw materials. The synthesis was conducted at 1400°C for 1 h under a pressure of 30 MPa. Because elemental powder Al is more reactive than Al_4C_3, this process can be accomplished at lower temperature and in less time than the processes introduced by Barsoum. It also demonstrated the advantages of simple procedure and high purity in the final product as well as low cost. So we adopted a process in our research similar to that used by Wang for the synthesis of Ti_2AlC bulk material by hot pressing of TiC, Ti, Al and active carbon powder mixtures. TiC and active carbon were used because it has been confirmed that TiC is the intermediate phase to synthesize Ti_2AlC [10] and active carbon has a larger reactivity than graphite. We think Ti_2AlC bulk material could be prepared by hot pressing of TiC/Ti/Al/C powder mixtures and there was no such report at present.

2. Experimental procedures

TiC, Ti, Al and active carbon were used as raw materials. The purity and average particle size of the initial

TABLE I Characteristics of raw materials: TiC, Ti, Al and C

Raw materials	TiC	Ti	Al	C
Purity (wt%)	99.8	99.0	99.8	99.0
Average size (μm)	4.5	10.6	12.8	13.2

powders are shown in Table I. Raw materials with a composition of 0.5TiC/1.5Ti/1.0Al/0.5C (in molar) were weighted and ground for 24 h and then put in a graphite die with a diameter of 16 mm. The graphite die was placed in a hot pressing furnace and heated at 5°C/min to 300°C and then heated at 60°C/min to the final processing temperature (1300, 1400 and 1500°C) holding for 60, 120 or 180 min. At last samples were cooled slowly in the furnace. During the whole process the powder mixtures were pressed under a pressure of 30 MPa. The chamber was filled with Ar before and after sintering. The resultant samples were 4–6 mm thick.

The surface layers of the samples synthesized by hot pressing at different temperatures with different soaking times were machined to avoid contamination from the graphite mold. The samples were then polished with 5 μm SiC grit sheet for XRD analysis (D/MAX-RB, RIGAKU Corporation, Japan). The fracture surfaces of the samples were microstructurally characterized using a scanning electron microscope (SEM) (JSM-5610LV, Jeol Ltd., Japan). The density of the samples was measured according to Archimedes law. The micro-hardness was measured using a Leitz Micro-hardness Tester (Leitz Wetzlar, Germany) at 0.98 N with a loading time of 30 s. The hardness was calculated by averaging at least 10 measurements.

3. Results and discussions

3.1. XRD patterns of samples hot pressed at different temperatures

Ti_2AlC and Ti_3AlC_2 usually co-exist with each other. Although many diffraction peaks of these two phases have very close 2θ values within the range of $10° < 2\theta < 70°$, we can distinguish between them with many methods. One is to distinguish the 2θ values of their strongest peaks. According to large amounts of XRD patterns of Ti_2AlC and Ti_3AlC_2 containing samples detected by the apparatus mentioned above, the 2θ value of the strongest peak of Ti_2AlC is higher than 39.26°, while that of Ti_3AlC_2 is lower than 39.22°.

Fig. 1 shows the phase makeup of samples prepared with different hot pressing temperatures and times from 0.5TiC/1.5Ti/1.0Al/0.5C powder mixtures.

It can be seen from Fig. 1 that hot pressing of the powder mixtures of 0.5TiC/1.5Ti/1.0Al/0.5C at 1300°C for 1 h resulted in the formation of Ti_2AlC, Ti_3AlC_2, TiC and Ti—Al compounds (Fig. 1a) and the peak intensity of Ti_2AlC was the strongest indicating Ti_2AlC was the main crystal phase. When powder mixtures were hot pressed at the same temperature but for 2 h, XRD pattern was similar to the previous one. The main crystal phase was still Ti_2AlC without obvious increment of peak intensity. Similarly, the peak intensities of Ti_3AlC_2, TiC and Ti—Al compounds did not change significantly (Fig. 1b). This shows apparently that increasing hot pressing time from 1 to 2 h at 1300°C could not largely increase the amount of Ti_2AlC, nor lower the amounts of Ti_3AlC_2, TiC and Ti—Al compounds. So we decided to increase the hot pressing temperature. It is found that only peaks of Ti_2AlC desired were in the XRD patterns when the powder mixtures of 0.5TiC/1.5Ti/1.0Al/0.5C were hot pressed at 1400°C for 1 and 3 h (Fig. 1c and d). When the powder mixtures were hot pressed at higher temperature of 1500°C for 1 h, peaks of Ti_3AlC_2 appear again (Fig. 1e), so the hot pressing temperature for the preparation of Ti_2AlC should be lower than 1500°C when using TiC, Ti, Al and active carbon as raw material.

It is indicated that Ti_2AlC can be prepared at 1400°C by hot pressing of 0.5TiC/1.5Ti/1.0Al/0.5C powder mixtures at 1400°C for 1 or 3 h. At lower temperature of 1300°C the speed of reaction forming Ti_2AlC

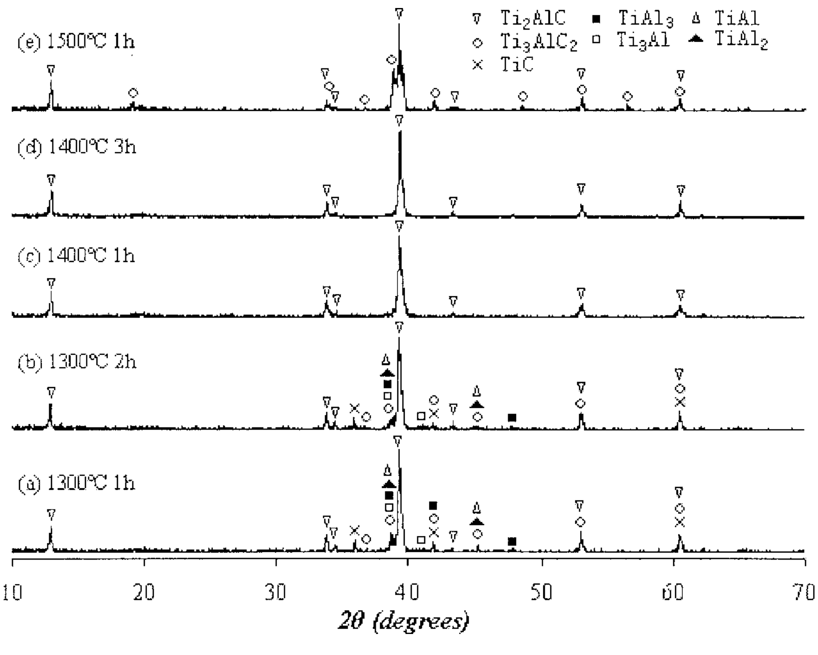

Figure 1 XRD patterns of samples hot pressed at different temperatures.

was very slow and a larger amount of other phases still existed in sample by hot pressing of the powder mixtures at 1300°C for 2 h. Excessively increasing the temperature to 1500°C resulted in the formation of Ti_3AlC_2 in 1 h and is not suitable for the preparation of Ti_2AlC.

It is generally acknowledged that Ti_2AlC is formed by the diffusion of carbon in firstly-formed Ti—Al compounds [11], so increasing heating temperature is more effective than elongating heating time in order to accelerate the reaction to form Ti_2AlC. Moreover, most Ti—Al compounds melt at about 1350°C [11], so the diffusion rate changes sharply near 1350°C. When the powder mixtures of 0.5TiC/1.5Ti/1.0Al/0.5C were hot pressed at 1300°C, the diffusion rate was very slow and the reaction to form Ti_2AlC was not over in 2 h. At 1400°C, the diffusion rate was very high and the reaction finished in 1 h. However, further increasing the hot pressing temperature to 1500°C resulted in the formation of Ti_3AlC_2 (Fig. 1e). It has been confirmed by Wang that Ti_2AlC reacts with TiC, Ti_3AlC and graphite and transforms to Ti_3AlC_2 in the temperature range 1400–1500°C [11]. Pietzka also found that Ti_2AlC melts incongruently at 1625 ± 10°C decomposing into liquid and TiC [12]. These two researches are not completely consistent with each other but they clearly shows that Ti_2AlC is not stable at high temperature. Since no TiC, Ti_3AlC or graphite except Ti_2AlC was detected in sample prepared at 1400°C by XRD within the limitation of the apparatus, there should be other route through which Ti_2AlC changes to Ti_3AlC_2. Ti_2AlC has similar crystal structure with Ti_3AlC_2. In Ti_2AlC, close-packed aluminum planes separate one layer of edge-shared Ti_6C octahedra, while in Ti_3AlC_2 every two layers of Ti_6C octahedra are interleaved with a layer of pure Al atoms. Besides, the bonding in Ti—Al is weaker than Ti—C bonding, so it is reasonable to suppose that some aluminum atoms broke away from the Ti—Al bonding, evaporated and lost as temperature was further raised to 1500°C, leading to the formation of Ti_3AlC_2.

TABLE II Density, porosity, and micro-hardness of different samples

Hot pressing temperature and time	ρ (g/cm^3)	Relative density	Micro-hardness (GPa)	Note
1300°C, 1 h	3.72	–	–	Porous
1300°C, 2 h	3.80	–	–	Porous
1400°C, 1 h	3.95	96.1%	5.58	–
1400°C, 3 h	4.03	98.0%	4.75	–
1500°C, 1 h	4.23	–	–	–

Sample density was also measured and results are showed in Table II.

It is revealed from Table II that the density of sample hot pressed at 1300°C for 1 h was 3.72 g/cm^3. When hot pressed at this temperature for 2 h, the density only slightly increased to 3.80 g/cm^3 and was still porous. When hot pressed at 1400°C for 1 h the density sharply increased to 3.95 g/cm^3, which is 96.1% of theoretical value. And if hot pressing time increased to 3 h at such temperature, it arrived 4.03 g/cm^3, i.e., 98% of theoretical density. If hot pressed at 1500°C, sample density was 4.23 g/cm^3, which is higher than the theoretical density of pure Ti_2AlC 4.11 g/cm^3, and sample had no porosity. This reveals that a new phase that has a theoretical density higher than that of pure Ti_2AlC appeared in the sample hot pressed at 1500°C. XRD pattern shows this new phase was Ti_3AlC_2 (theoretical

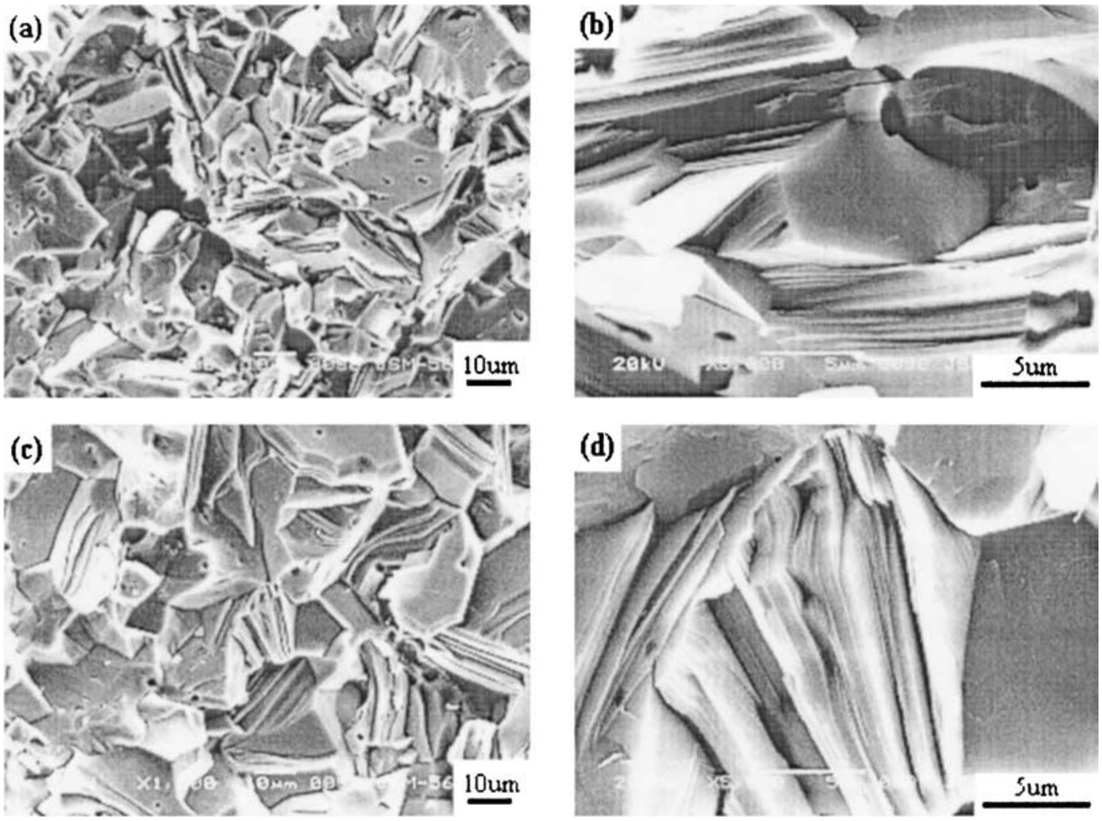

Figure 2 SEM photographs of the fracture faces of samples hot pressed at 1400 for 1 h (a) and (b) and 3 h (c) and (d).

density of Ti_3AlC_2 is 4.25 g/cm^3, larger than that of pure Ti_2AlC).

According to above analysis, it is sure that Ti_2AlC can be prepared by hot pressing of 0.5TiC/1.5Ti/1.0Al/0.5C powder mixtures at 1400°C for 1 and 3 h.

3.2. Microstructure of Ti_2AlC samples

The microstructures of Ti_2AlC samples are shown in Fig. 2. It is clear that samples synthesized by hot pressing of the powder mixtures of 0.5TiC/1.5Ti/1.0Al/0.5C at 1400°C for 1 and 3 h fully consisted of laminated and homogeneously distributed grains. It has been confirmed that Ti_2AlC has laminated microstructure due to its layered crystal structure [13]. So, combining with the XRD patterns (Fig. 1c and d), it is true that the grains in these two samples were Ti_2AlC. When hot pressed at 1400°C for 1 h, the laminated grains were 10–25 μm in length and 6 μm in thickness (Fig. 2a). Increasing the hot pressing time to 3 h at 1400°C resulted in the growth of laminated grains with a length of about 30 μm and a thickness of 15 μm (Fig. 2c). Also it can be seen that when hot pressed at 1400°C for 1 h, there existed a large number of pores. The pore size was large and irregular. When hot pressed at 1400°C for 3 h, the porosity decreased. The pore size was also reduced and became regularly circular. This is consistent with the density shown in Table II. That is increasing the hot pressing time at 1400°C from 1 to 3 h resulted in the increase of sample density from 3.95 to 4.03 g/cm^3. Due to the existence of pore, density of sample hot pressed at 1400°C for 3 h was still lower than the theoretical density of Ti_2AlC.

Micro-hardness of samples synthesized at 1400°C for 1 and 3 h were also measured and they were 5.58 and 4.75 GPa respectively (shown in Table II). These values were within the range of 3–6 GPa reported by Barsoum [7, 8].

4. Conclusions

Bulk polycrystalline samples of Ti_2AlC were synthesized by hot pressing of TiC, Al, Ti and active carbon at 1400°C for 1 and 3 h under a pressure of 30 MPa, with 96.1 and 98% of theoretical density respectively. The micro-hardness of these two Ti_2AlC samples was 5.58 and 4.75 GPa against the indentation load of 0.98 N, respectively. At lower temperature of 1300°C, the speed of the reaction forming Ti_2AlC was slow and larger amounts of other phases still existed in sample by hot pressing of the powder mixtures at 1300°C for 2 h. While at higher temperature of 1500°C, Ti_2AlC transformed to Ti_3AlC_2. So these two temperatures are not suitable for the fabrication of Ti_2AlC by hot pressing.

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