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Effects of TiN addition on the properties of hot pressed TiN–Ti/Al_2O_3 composites

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ABSTRACT

TiN–Ti/Al_2O_3 composites of varying TiN content (0–20 vol%) were prepared by vacuum hot-pressing sintering at different temperatures (1400 °C and 1500 °C) to investigate how TiN affected the mechanical properties and electrical conductivity of the composites. Sintered samples with added TiN exhibited better performance than those without it. The sample with 20 vol% TiN sintered 1500 °C had an optimal relative density of 99.49, Vickers hardness of 14.94 GPa, flexural strength of 321.55 MPa, and electrical resistivity of 1474.7 μΩ cm. However, this increased temperature did not improve the best sample resistivity of 930.3 μΩ cm, which was obtained at 1400 °C. Form SEM images and XRD patterns, the positive effect of TiN on composite mechanical properties may be ascribed to its good performance of high hardness and strength, a decrease of the brittle intermetallic phase, the form of $AlTi_3N$, and the impact of the fine-grained strength of the TiN phase.

1. Introduction

Cermet materials have attracted wide attention because their properties originate from both metal and ceramic materials, and include wear and corrosion resistance, high toughness, and strength [1–4]. As one of the most commonly-used high-temperature structural ceramics, Al_2O_3 is widely used in the semi-conductor, aerospace, and military industries due to its high hardness and good resistance to high temperature, corrosion, and wear [5–7]. On the other hand, metal Ti has been used in the aerospace, marine, and medical fields since it is tough, ductile, and electrically-conductive [8,9]. Most importantly, the two materials are physically and chemically compatible and share similar thermal expansion coefficients. Therefore, they meet the requirements for preparing Ti/Al_2O_3 cermet, popular in aerodynamic-engine and other automotive applications [10–12]. Unfortunately, in long-term studies of Ti/Al_2O_3 composites, intermetallic compounds of Ti–Al such as TiAl and Ti_3Al are always found. These are characterized by low fracture toughness at room temperature and low oxidation resistance at elevated temperatures, significantly restricting the application of Ti/Al_2O_3 [13–17].

To solve this problem, interface reaction control in Ti–Al materials has been investigated in depth. D. Pilone [13] and Liu et al. [18] reported that Cr, Si, Nb, Y, and W can be alloyed with Ti–Al to reduce the production of Ti–Al compounds by generating other substances. Ai et al. [19] showed that Ti–Al composites could be reinforced by Al_2O_3 and Nb_2O_5. Compound Al-$TiAl_3$ materials have also been prepared by uniform droplet spraying as described by Wang [14]. Excessive production intermetallic Ti–Al compounds can also be suppressed by adding metals such as Nb or metal oxides such as Y_2O_3 [20]. For instance, Wu et al. prepared laminar Ti/Al_2O_3 composites by casting method [21]. In addition, Nb, CeO_2, and Y_2O_3 were doped to reduce the diffusion of atoms at the interface of Ti/Al_2O_3 composites to restrain the formation of intermetallic Ti–Al compounds on the basis of the lamellar material, by Liu et al. [22,23]. Clearly, despite much effort, the brittleness of intermetallic Ti–Al compounds remains an open issue. Under these circumstances, we find that TiN has long been considered to be ideal in the applications such cutting tools, wear-resistant materials, decorative materials and electrodes owing to its high hardness, beautiful golden color, high chemical stability, and good electrical conductivity [24–26]. Simultaneously, TiN is often used to toughen and strengthen Al_2O_3 because of its effective pinning. Thus, we hypothesize that when TiN is introduced into Ti/Al_2O_3 composites, TiN may not only toughen and enhance the composites, but also reduce the generation of Ti–Al intermetallic compounds by combination with N. To date, many studies have centered on TiN, but none has explicitly focused on its effect on TiN–Ti/Al_2O_3 composites. Therefore, the impact of TiN on the mechanical properties and microstructure of TiN–Ti/Al_2O_3 is studied here, and the changes in conductivity and phase with increasing TiN are also characterized.

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Table 1
Chemical composition of group A samples (wt%).

Samples	Ti (vol%)	Al_2O_3 (vol%)	TiN (vol%)
A0	40	60	–
A1	40	58	2
A2	40	56	4
A3	40	54	6
A4	40	52	8
A5	40	50	10
A6	–	60	40

Table 2
Chemical composition of group B samples (wt%).

Samples	Ti (vol%)	Al_2O_3 (vol%)	TiN (vol%)
B0	40	60	–
B1	35	60	5
B2	30	60	10
B3	25	60	15
B4	20	60	20
B5	–	60	40

2. Experimental procedures

In this work, commercially available Al_2O_3 (99.9% pure, 1.5 μm), Ti (99.9% pure, 20 μm) and TiN (99.5% pure, 1 μm) from ST-NANO C o., Ltd. (Shanghai, China) were used as raw materials. In raw Al_2O_3 powder, α-Al_2O_3 accounts for the largest proportion. The experiment was divided into two groups, and the specimen design is summarized in Tables 1 and 2, respectively. Each group includes a TiN/Al_2O_3 sample in order to explore the reaction between Ti, TiN, and Al_2O_3. The TiN–Ti/Al_2O_3 composites were prepared as follows. After weighing, powders were mixed with a planetary ball mill (XQM-2, China) in an ethanol bath (99.7% pure) for 2 h at a milling speed of 200 rpm with a ball-to-powder weight ratio of 2:1. Then, the slurry was dried at 70 °C for 24 h in a vacuum oven. The dry powder was then placed into a graphite mold and sintered by vacuum hot-pressing (VVPgr-80-2300, Shanghai Haoyue, China). Sintering was performed with temperature rise of 10 °C/min (0–1200 °C), and 5 °C/min (1200–1500 °C), at which time the sintering temperature was held at 1400 °C (group A) and 1500 °C (group B) for 1.5 h under a load of 30 MPa. Lastly, sintered samples were removed when the temperature had naturally dropped to about 100 °C, after which the samples were cut, ground, and polished.

The relative densities of the samples were determined by the Archimedes method. Using the three-point bending method, the flexural strength of the treated specimens was measured by an electromechanical testing machine (CMT5504, MTS Systems, China) at room temperature with a crosshead speed of 0.5 mm/min and span of 30 mm, with specimens sizes limited to 3 mm × 4 mm × 35 mm. The microhardness was obtained with a Vickers hardness tester (HV-10001S, China) at room temperature with a load of 1000 gf and indentation time was maintained for 15 s. Phase analysis of the samples was performed using an X-ray diffraction analyzer (D8-ADVANCE, Germany) with Cu-Kα radiation, while the microstructure and elemental distributions of the composites were further analyzed with a scanning electron microscope (FEI QUANTA FEG 250, United States), and an electron probe micro-analyzer (Shimadzu EMPA-1600, Japan). In addition, the electrical resistivity was measured using the DC four-probe method with a current-reversal technique [27–29]. All characterization and tests were performed at room temperature.

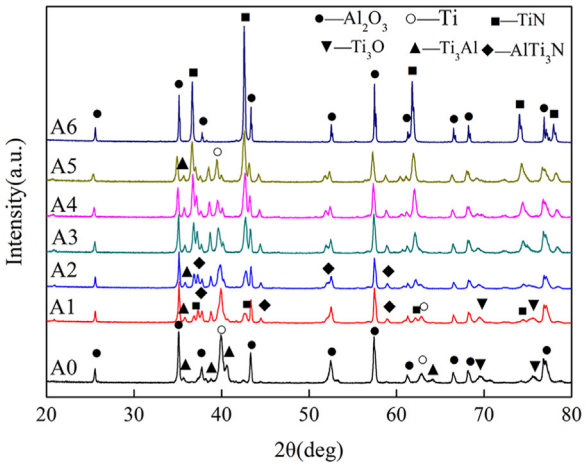

Fig. 1. XRD patterns of group A experiment.

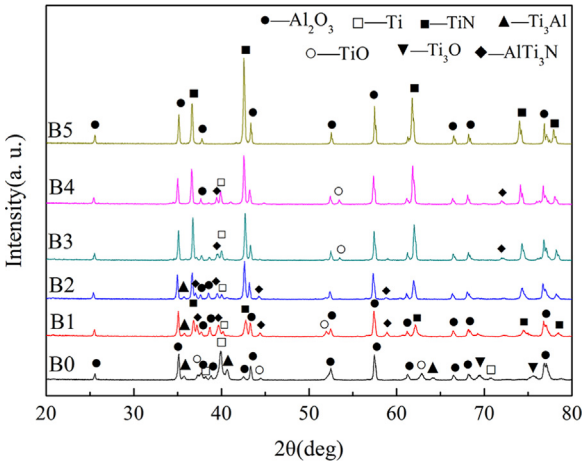

Fig. 2. XRD patterns of group B experiment.

3. Results and discussion

3.1. Effect of TiN on phase composition of TiN–Ti/Al_2O_3 composites

The results of X-ray diffraction analyses performed to determine the phase constitution of the TiN–Ti/Al_2O_3 composites are shown in Figs. 1 and 2. The new phase $AlTi_3N$ appeared with the addition of TiN, and the diffraction peaks of the TiN phases became stronger with increasing TiN content. No reactions occurred between TiN and Al_2O_3 for no other phase existed after sintering, as shown at points A6 and B5. As shown in Fig. 1 (A0–A5), the amount of Ti_3O gradually reduced with increasing TiN content, because the oxygen diffusion was hindered by the addition of TiN. From A0 to A4, however, the formation of $AlTi_3N$ increased gradually, stabilizing at A4 and A5. Meanwhile, the amount of Ti_3Al decreased when 2 vol% of TiN was added, as shown in Fig. 1 A1, remaining stable as additional TiN was added. From this, the production of $AlTi_3N$ requires two procedures: first, react Ti with Al_2O_3 to produce Ti_3Al, then combine Ti_3Al with N to generate $AlTi_3N$. This process also is responsible for reducing the amount of Ti_3Al.

As shown in Fig. 2, in contrast to samples from group A samples, TiO was found in group B samples sintered at 1500 °C. The amount of TiO decreased until eventually becoming zero as the amount of TiN increased, in line with the trend of Ti_3O. The reduction of TiO and Ti_3O should be attributed to the decrease of Ti, and the hindering effect of TiN on the diffusion of O elements. In group B, Ti was reduced due to the increased TiN, lowering the Ti_3Al. Moreover, a portion of the Ti_3Al combined with N to generate $AlTi_3N$. Therefore, the increased TiN led