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Oxygen scavenging, grain refinement and mechanical properties improvement in powder metallurgy titanium and titanium alloys with CaB_6

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ABSTRACT

The effect of calcium hexa boride (CaB_6) on microstructure and mechanical properties of powder metallurgy CP-Ti and Ti-6Al-4 V was studied. CaB_6 can scavenge the solid solution O during sintering, producing Ca-Ti-O and TiB second phases. These Ca-containing particles precipitate in the grain boundary to inhibit grain growth, resulting in the formation of equiaxed α grain in CP-Ti and a fine and homogeneous basket-weave structure in Ti-6Al-4 V. Compared to CP-Ti, the α phase of Ti-1CaB_6 reduces from 178 μm to 36 μm. With respect to Ti-6Al-4 V, the α + β lamellae length reduces from 203 to 38 μm. The sintered relative density is also improved with O scavenging. The relatively density increases to 99.3% in Ti-0.2CaB_6 and 98.8% in Ti-6Al-4 V-0.1CaB_6. The same reason may also account for the improved ductility. Overall, an addition of 0.2 wt% CaB_6 in CP-Ti and 0.1 wt% CaB_6 in Ti-6Al-4 V can obtain better comprehensive tensile properties (UTS = 665 MPa, YS = 604 MPa, EL. = 15% for Ti-0.2CaB_6; UTS = 944 MPa, YS = 903 MPa, EL. = 9% for Ti-6Al-4 V-0.1CaB_6).

1. Introduction

Due to its near-net-shape capabilities, homogenous microstructures, and isotropic properties, powder metallurgy (PM) technology has long been regarded as a promising method to reduce the cost of Ti and Ti alloys [1]. But, one inevitable issue with the PM Ti alloys is that interstitial oxygen exists, which significantly affects not only ductility but also the stress-corrosion cracking resistance and fracture toughness [2–4]. For example, the tensile elongation of Ti-6Al-4 V drops from over 10% to below 5% once the O content exceeds 0.33 wt%, and further to <2% when the O content is obove 0.45 wt% [5]. For PM Ti alloys, they usually contain a much higher level of O than conventional ingot metallurgy (IM) Ti alloys due to the inevitable contact with air of Ti powder. Now, most low-cost hydride–dehydride (HDH) Ti powder products contain over 0.25 wt% O. The subsequent powder treatment and sintering process will easily increase 0.1 wt% O, exceeding the critical value of 0.3 wt% (the ASTM Standard B988–13 for PM Ti) for most Ti alloys. Therefore, mitigating the detrimental effect of O in PM Ti plays a key role in preparation of low-cost and high-performance Ti alloys.

Rare earth (RE) elements have been long known as the efficient scavengers of O for both IM and PM Ti alloys due to their higher chemical affinity with O [6–8]. RE elements are usually introduced into PM Ti alloys as the form of RE hydride [9] (YH_2, LaH_2), RE-containing compounds like borides [10,11] (LaB_6) or silicides [12] ($CeSi_2$) and some kinds of RE master alloy [13] (Al-Nd). But, due to the cost and scarcity of RE, the most pressing task is to seek a new compound as the O scavenger to replace the RE for the preparation of low-cost and high-performance Ti alloys.

The calcium (Ca) and its compounds were used in the deoxidation of Ti. For instance, the O content contained in the powder was decreased from 2500 ppm to 920 ppm with the use of a non-contact deoxidation pot and Ca vapor [14]. But, elemental Ca is unstable and low-melting-point. It is hard to be introduced in Ti alloys. Among the Ca compounds, calcium hexa boride (CaB_6) appears to be one such promising candidate. Firstly, it is commercially available and very stable at room temperature. Then, it is cheaper than all forms of RE-containing compounds, while O has a higher chemical affinity with Ca than that with RE. Finally, B would enhance the sintered density and refine the grain, and the in-situ TiB is an effective reinforcement phase for Ti alloys [15].

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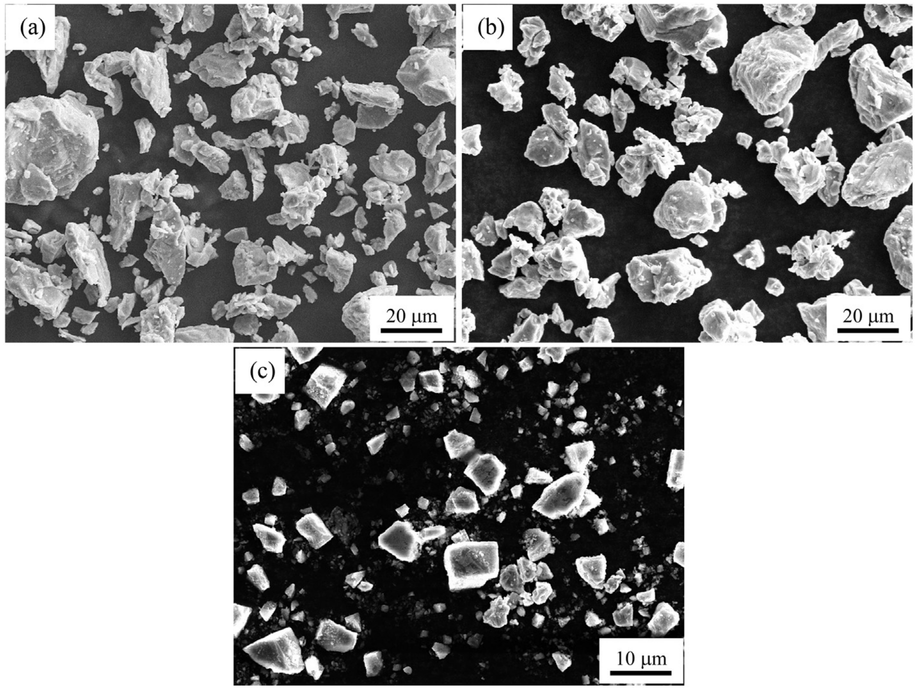

Fig. 1. Scanning electron micrographs of: (a) HDH Ti powder; (b) HDH Ti-6Al-4 V powder; (b) CaB_6 powder.

To date, no related reports about the introduction of CaB_6 in PM Ti alloys. It is unknown if CaB_6 will be able to scavenge O from the Ti powder and how the mechanical properties will respond accordingly. This paper presents a systematic study of the effects of CaB_6 in CP-Ti and Ti-6Al-4 V on the sintering density, O scavenging, microstructural evolution and mechanical properties.

2. Experimental procedure

The raw materials were HDH Ti powder (99.5% purity, 0.35 wt% O, −325 mesh), Ti-6Al-4 V powder (99.5% purity, 0.4 wt% O, −325 mesh), CaB_6 powder (99.9% purity, $D_{10} = 0.64$ μm, $D_{50} = 5$ μm, $D_{90} = 18.6$ μm), B powder (99.9% purity, $D_{50} = 5$ μm). The SEM micrographs of the powders are shown in Fig. 1, in which both HDH Ti and Ti-6Al-4 V powder have the irregular morphology with rough and uneven surface, while CaB_6 powder has a regular cubic shape. HDH Ti and Ti-6Al-4 V powder were separately mixed with various amounts of CaB_6 (x, y = 0.0, 0.1, 0.2, 0.4, 0.6, 1 wt%) powder. This was done by ball milling for 5 h using SPEX-8000 mixer/mill. For comparison, the equivalent B was also added to investigate the relative density and microstructure. After being compacted by cold isostatic pressing (CIP) at 200 MPa, the green compacts were vacuum-sintered at 1300 °C for 120 min under a vacuum of 10^{-3}–10^{-2} Pa, heating at 2 °C/min and cooling with furnace.

The sintered samples' densities (ρ_s) were measured using the Archimedes method according to the ASTM B328. The relative density values were calculated as ρ_s/ρ_n*100, where ρ_n is the nominal density of the Ti-xCaB_6 and Ti-6Al-4 V-yCaB_6. Room temperature tensile tests were conducted using an AGI-250KN testing machine, at the strain rate of 1×10^{-3} s^{-1}, according to ASTM E8-08. Five tensile test specimens for each processing condition were used to ensure the repeatability. Vickers hardness measurements were carried out in a Wilson-Wolpert DIGI-TESTOR 930 machine using a load of 20 kg. X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα target, 40 kV and 40 mA, 30°– 80°) was performed for phase identification of the as-sintered samples. The sintered microstructures, fracture surfaces, and surface morphology of the powder were analyzed using optical microscopy (OM, Axio Imager M2 m), and scanning electron microscopy (SEM, Philips LEO-1450) equipped with energy-dispersive spectroscopy (EDS, Model JEOL, JEOL Ltd., Tokyo, Japan). The α grain size in Ti-xCaB_6 and the length and thickness of α lath in Ti-6Al-4 V-yCaB_6 (the aspect ratio of α lath is the ratio between α lath length and thickness) were both evaluated in low magnification OM images by an image analyzer (UTHSCSA Image Tool).

3. Results and discussions

3.1. Relative density

The relative densities of the compacts after CIP are approximately 84.6 ± 1.3%. The relative densities of the sintered samples are shown in Fig. 2. The relative density of Ti-xCaB_6 increased first with increasing CaB_6 content from 0 to 0.2 wt%, reaching its maximum value 99.3%, then decreased afterwards. The SEM images of Ti and Ti-0.2CaB_6 are shown in Fig. 3(i) and Fig. 3(j), respectively. There are a few pores about 2–12 μm distributing in the Ti matrix, but no visible pores are shown in the Ti-0.2CaB_6. But for Ti-6Al-4 V-yCaB_6, the relative density decreased when the addition of CaB_6 exceeded 0.1 wt%. And the maximum value is about 98.8%. The results confirm that the addition of CaB_6 is effective in enhancing the sintered densities of CP-Ti, Ti-6Al-4 V, but the appropriate addition level is different for CP-Ti and Ti-6Al-4 V. The effect of the addition of elemental B on the relative densities is also shown in Fig. 2. It shows that the relative densities of CP-Ti and Ti-6Al-4 V both increase with B content increasing. When B content exceeds 0.4 wt% in Ti and 0.3 wt% in Ti-6Al-4 V, the relative densities decrease slightly, still remaining above 98%. This tendency has been reported in the literature [16] and it is closely connected to the decreased solidus temperature. With the additions of ≤0.2 wt% CaB_6 for CP-Ti and ≤ 0.1 wt% CaB_6 for Ti-6Al-4 V, the sintered samples obtain a higher relative density. Thus, the improvement of relative density not only comes from B, but also from the Ca included in the CaB_6. The Ca can remove a part of O on the Ti surface by generating Ca-Ti-O complex oxides,