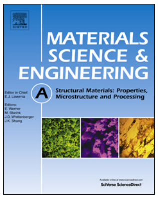
Materials Science & Engineering A 618 (2014) 447–455

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea



The effect of lanthanum boride on the sintering, sintered microstructure and mechanical properties of titanium and titanium alloys

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ARTICLE INFO

Article history:
Received 26 May 2014
Accepted 28 August 2014
Available online 6 September 2014

Keywords:
Powder metallurgy
Sintering
Titanium alloys
Grain refinement

ABSTRACT

An addition of $\leq$0.5 wt% lanthanum boride (LaB_6) to powder metallurgy commercially pure Ti (CP-Ti), Ti–6Al–4V and Ti–10V–2Fe–3Al (all in wt%) resulted in improved sintered density, substantial microstructural refinement, and noticeably increased tensile elongation. The addition of LaB_6 led to scavenging of both oxygen (O) and chlorine (Cl) from the titanium powder during sintering, evidenced by the formation of La_2O_3 and $LaCl_xO_y$. The pinning effect of La_2O_3, $LaCl_xO_y$ and TiB inhibited prior-β grain growth and resulted in subsequent smaller α-laths. The formation of nearly equiaxed α-Ti phase is partially attributed to the nucleation effect of α-Ti on TiB. The improved sintered density was caused by B from LaB_6 rather than La, while excessive formation of La_2O_3 and TiB with an addition of $>$0.5 wt% LaB_6 resulted in a noticeable decrease in sintered density. The improved tensile elongation with an addition of $\leq$0.5 wt% LaB_6 was mainly attributed to the scavenging of oxygen by LaB_6, partially assisted by the improved sintered density. However, an addition of $>$0.5 wt% LaB_6 led to the formation of large La_2O_3 aggregates and more brittle TiB whiskers and therefore decreased tensile elongation. Balanced scavenging of O is thus important. The optimal addition of LaB_6 was 0.5 wt% but this may change depending on the powder size of the LaB_6 to be used.

1. Introduction

The costly manufacturing process based on the ingot metallurgy approach hinders the wider application of titanium (Ti) alloys, despite their outstanding properties [1]. The simple cold-compaction-and-pressureless-sinter powder metallurgy (PM) process offers a promising cost-effective approach to the fabrication of Ti alloys in near-net shaped product forms [1,2]. The price of Ti powder, which depends largely on its oxygen content (typically $>$\$120/kg for $\leq$0.15 wt%O), is a critical factor that affects the cost affordability of PM Ti components for large tonnage structural applications. In addition, oxygen significantly affects the mechanical properties [1,3–7]. For instance, increasing O content from 600 ppm to 1200 ppm leads to almost total brittleness of aged Ti–8Al (in wt% throughout) of which the tensile elongation drops from 20% to 1% [8]. In the context of powder metallurgy (PM) Ti alloys, the critical O content for as-sintered Ti–6Al–4V has been determined to be around 0.33% beyond which the tensile elongation decreases from more than 10% to less than 5% with 0.35% O and further to less than 2% with about 0.45% O [6,7]. To ensure sufficient ductility for structural applications, the ASTM Standard Specification B988-13 for PM Ti structural components has specified that the maximum O content in PM Ti–6Al–4V is limited to 0.3%. Control of the influence of oxygen thus plays a key role in enabling the development of low-cost high performance PM Ti alloys.

Rare earth (RE) elements have proved to be effective scavengers of O for both PM Ti alloys [9–17] due to their higher chemical affinity for O than Ti. A brief review of the scavenging of oxygen from PM Ti by an addition of RE can be found in Ref. [16]. Among various forms of RE additions, LaB_6 is an attractive candidate for PM Ti for the following reasons:

- La is inexpensive. In fact, it is cheaper than the HDH Ti powder made from Ti sponge and also cheaper than Sn and much cheaper than Mo and V, which are common alloying elements for Ti. In addition, LaB_6 is stable at room temperature (RT);
- enlightened by previous studies of yttrium [9,10] and yttrium oxide [18] in PM Ti, La or La_2O_3 has the potential to scavenge Cl from PM Ti; and
- B enhances the sintering and refines the microstructure of PM Ti materials and the resultant TiB is an effective reinforcement phase for Ti alloys [7,19].

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http://dx.doi.org/10.1016/j.msea.2014.08.080
0921-5093/

Table 1
Powder materials used.

Powder materials	Particle size (μm)	Purity (%)	O content (wt%)	Manufacturer
HDH Ti	≤ 63	99.4	0.25	Kimet Special Metal Powder Co. Ltd., China
66.7V–13.3Fe–20Al master alloy	≤ 45	99.5	0.03	Baoji Jia Cheng Rare Metal Materials Co. Ltd., China
58V–42Al master alloy	≤ 45	99.5	0.05	Baoji Jia Cheng Rare Metal Materials Co. Ltd., China
LaB_6	≤ 45	99.5	–	Alfa Aesar®, USA
Aluminium	~ 3	99.7	–	Aluminium Powder Company Ltd., England
Boron	~ 1	~ 95	–	Strem Chemicals

It should be noted that LaB_6 has been introduced to a PM Ti–1.5Fe–2.25Mo alloy previously [12] and an addition of 0.15 wt% LaB_6 increased the tensile elongation by 60% and the tensile strength by 15%. These results show the effectiveness of introducing LaB_6 to PM Ti for improved ductility and strength. However, the introduction of $>0.15\%$ LaB_6 led to a decrease in both the density and tensile ductility of the as-sintered Ti alloys. No detailed mechanism was provided about the unexpected observations. The ductility of different types of Ti alloys shows a different sensitivity on the oxygen content, e.g., the ductility of CP-Ti drops from 37.1% to 15% with increasing oxygen content from 0.07% to 0.12% while a significant drop occurred for $\alpha+\beta$ Ti–6Al–4V alloy only when the oxygen content increased to 0.32% [1,2]. This implies that the optimal addition level of RE changes for different types of Ti alloys. On the other hand, although enhanced sintering densification by LaB_6 was reported, microstructural changes including the modification of α-Ti lath and the distribution of the reaction products in the microstructure remain unclear. In addition, the densification mechanism and microstructure modification mechanism are still unknown. A recent detailed study of the addition of YH_2 powder to PM CP-Ti and Ti alloys revealed that yttrium scavenged both O and chlorine (Cl) from the Ti powder during sintering [9]. It is unknown if LaB_6 can similarly scavenge both O and Cl. These details are important for capitalising on the scavenging effect of LaB_6 for the fabrication of low-cost high performance PM Ti alloys.

This paper presents a systematic study of the effect of LaB_6 on the sintering densification, impurity scavenging, microstructural refinement and mechanical properties of CP-Ti (Grade 2), Ti–6Al–4V and Ti–10V–2Fe–3Al. The densification mechanism, microstructure refinement mechanism and the influence of scavenging of O and Cl on the mechanical properties are also discussed in detail.

2. Experimental procedure

Table 1 summarises the powder materials used. CP-Ti, Ti–6Al–4V and Ti–10V–2Fe–3Al were selected for their commercial importance. Elemental Al powder and a 58V–42Al master alloy powder were used together to balance the composition of Ti–6Al–4V. Elemental B powder was used to distinguish between the roles of La and B introduced as LaB_6 in the densification and refining processes.

The powder mixing, cold compaction and tensile sample preparation were similar to those described elsewhere [11]. The uniaxial cold compaction was performed under 600 MPa with the resulting green density of all the samples being around 78% of the theoretical density (TD). Isothermal sintering was performed at 1350 °C for 120 min in a tube furnace under a vacuum of 10^{-3}–10^{-2} Pa, with heating and cooling both at 4 °C/min. The sintered density was measured from three samples using the Archimedes method according to the ASTM standard B328.

Differential scanning calorimetry (DSC, Model Netzsch STA 409CD, Germany) was used to examine the stability of LaB_6 during heating to 1350 °C at 10 °C/min in high purity flowing argon. Changing the heating rate from 4 °C/min to 10 °C/min had no noticeable effect on the sintering behaviour [20]. Samples cut from tensile bars were polished using 50 nm colloidal alumina for microstructural examination. Polished samples of as-sintered CP-Ti were etched with Kroll's etchant to reveal the grain boundaries. The microstructure was analysed using scanning electron microscopy (SEM, Model JEOL 6460 L, Japan) equipped with energy-dispersive spectroscopy (EDS, Model JEOL, Japan). X-ray diffraction (XRD, Rigaku D/max III, Japan, Cu Kα target) was used to identify the phase composition. An Image-Pro Plus 5.0 Software statistical tool was used to quantify the grains size of the as-sintered microstructure. The average prior-β grain size was measured from 500 grains while the average length of the α-Ti laths and the average equiaxed α-Ti grain size in as-sintered Ti–6Al–4V and Ti–10V–2Fe–3Al were measured from 1000 α-Ti laths and 1000 equiaxed grains, respectively, from about 100 micrographs in each case.

Tensile specimens (3 mm × 4.5 mm cross-section and 15 mm gauge length, see Fig. 1) were machined from as-sintered bars and tested on an Instron mechanical tester (Model 5054, USA) with a crosshead speed 0.5 mm/min, where a video extensometer was used to monitor the displacement. The oxygen and nitrogen contents of as-sintered tensile samples were analysed using a Leco Nitrogen/Oxygen Analyser (Model TC-136). Cl content was analysed using Ratio Beam Spectrophotometer (Model Hitachi U-1900, Japan).

3. Results

3.1. Sintered density

Fig. 2 shows the effect of the addition of LaB_6 on the relative sintered densities of CP-Ti, Ti–6Al–4V and Ti–10V–2Fe–3Al after sintering at 1350 °C for 120 min. Table 2 lists the theoretical and experimental density data. The relative sintered density increased with increasing LaB_6 content from 0 to 0.5% but decreased afterwards in each case. These results confirm that the addition of LaB_6 is effective in enhancing the sintered densities of CP-Ti, Ti–6Al–4V and Ti–10V–2Fe–3Al but the addition level should be less than 0.5%.

Also shown in Fig. 2 is the effect of the addition of elemental B, made equivalent to the addition of LaB_6, on the sintered densities of CP-Ti, Ti–6Al–4V and Ti–10V–2Fe–3Al after sintering at 1350 °C for 120 min. It is clear that the improvement of the sintered density by an addition of $\leq 0.5\%$ LaB_6 mainly stems from the introduction of B. However, at $>0.5\%$ LaB_6, the sintered density obtained from the addition of elemental B is consistently higher than that from the addition of LaB_6. Also, the difference increased with increasing addition of LaB_6 (see Fig. 2). This indicates that the introduction of La beyond 0.34% (equivalent to 0.5% LaB_6) actually decreased the sintered density in each case. It should be noted that the effect of the difference in particle size of the used LaB_6 and B on the sintered density can be negligible. Our previous work about the effect of another RE-containing compound ($CeSi_2$) has shown a good example: when $CeSi_2$ and Si with the same size were