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Impurity scavenging, microstructural refinement and mechanical properties of powder metallurgy titanium and titanium alloys by a small addition of cerium silicide

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ABSTRACT

A small addition (≤0.5 wt%) of cerium silicide ($CeSi_2$) to powder metallurgy (PM) commercially pure Ti (CP-Ti), Ti–6Al–4V and Ti–10V–2Fe–3Al (all in wt%) results in substantial microstructural refinement and noticeably improved ductility with marginally improved sintered density. $CeSi_2$ is unstable and decomposes between 1423 K and 1473 K. The Si goes into solid solution in β-Ti and is responsible for the improved sintered density while the Ce scavenges both oxygen (O) and chlorine (Cl) from the Ti powder and therefore improves tensile ductility. The resulting CeO_2 and $CeCl_xO_y$ particles generally exist along or close to the prior-β grain boundaries. The substantial microstructural refinement in terms of both the prior-β grain size and the subsequent α-Ti lath size is attributed to the grain boundary pinning effect of the CeO_2 particles. The optimum concentration of $CeSi_2$ is approximately 0.5 wt%, beyond which both the sintered density and tensile elongation drop with increasing addition of $CeSi_2$. $CeSi_2$ can be a practical form of Ce addition to PM Ti alloys for impurity scavenging, microstructural refinement and tensile ductility improvement.

1. Introduction

Powder metallurgy (PM) offers the potential for cost-effective fabrication of titanium (Ti) components for a wide range of applications [1–3]. Oxygen (O) is an important issue that affects this potential in terms of both the cost of production and the resulting mechanical properties. Recent studies have revealed that the tensile elongation of PM Ti–6Al–4V (all compositions are given in wt% herein) changed little with increasing oxygen content from 0.2 wt% to ~0.32 wt% [4,5] but dropped from >10% to <5% once the oxygen content exceeded ~0.32 wt%, and further to <2% when the oxygen content was >0.45 wt% [4]. The oxygen content of an as-sintered Ti alloy largely depends on the oxygen content of the Ti powder. Currently, most inexpensive hydride–dehydride (HDH) Ti powder products contain ≥0.25 wt% oxygen. The powder handling and sintering process can readily add an extra 1000 ppm of oxygen, exceeding the critical value of 0.32 wt%. Being able to effectively mitigate the detrimental effect of oxygen on ductility is thus important for the fabrication of low-cost high-performance Ti alloys using inexpensive HDH Ti powder.

The Ellingham diagram [6] indicates that at a typical sintering temperature of ≥1473 K for PM Ti, only rare earth (RE) elements are practical to scavenge oxygen from titanium. In the 1970s and 1980s, RE elements were widely introduced into Ti alloys by rapid solidification processing (RSP) [7–31] and the formation of RE oxides was investigated both theoretically and experimentally [27]. The RSP led to metastable supersaturation of RE and O in Ti. As a result, precipitation of fine RE oxides occurred during subsequent heat treatment through the scavenging of O by the RE elements. In the presence of excessive oxygen, the resulting RE oxides would evolve to the most stable stoichiometric particle [27]. The presence of these fine RE oxides enhanced the elevated-temperature strength by dispersion hardening of the final RSP product forms consolidated from powder, flake, ribbon, fiber, etc. However, the resulting tensile ductility was barely affected as the initial oxygen content in the Ti alloy ingot was already very low [14–18]; there was no need to scavenge the oxygen from a ductility perspective. In the 1990s, RE elements were introduced into PM Ti alloys in the form of RE-containing compounds (most notably as RE oxides) [32–34]. Because most RE oxides are not oxygen deficient, they fail to scavenge oxygen from the Ti powder. As a result, the resulting tensile elongation showed little improvement [32–34]. The benefits of using RE elements to improve the tensile ductility of as-sintered PM Ti alloys were first demonstrated by Liu and co-workers [35,36]. They introduced RE elements to PM Ti alloys in the form of a 60Al–40Nd (at%) master alloy powder and achieved substantially improved tensile ductility. Subsequently, Zhang et al. [37] mixed mechanically crushed neodymium (Nd)

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Table 1
Summary of rare earth (RE) additions to PM Ti alloys.

Addition form	Alloy (wt%)	Addition level (wt%)	Relatively sintered density (%)	UTS (MPa)	YS (MPa)	Elongation (%)
60Al–40Nd (at%) master alloy [22]	Ti–6Al–4V	0	~97	~1030	–	~2.5
		0.3	~97.5	~1050	–	~11
		0.8	~97.5	~990	–	~12
		1.2	~97.2	~940	–	~13
60Al–40Nd (at%) master alloy [22]	Ti–1Fe–1Mo–4.5Al	0	~97.2	~850	–	~1
		0.3	~97.9	~950	–	~2
		0.8	~97.7	~950	–	~3
		1.2	~97.7	~920	–	~5
LaH_2 [22,26]	Ti–1.5Fe–2.25Mo	0	~93	~685	~634	~4.8
		0.15	~94	~710	~650	~5
		0.3	~95	~740	~660	~8
		0.6	~95.9	~770	~690	~5.5
		1.2	~95.5	~760	~685	~5.4
		3.0	~95.2	~710	~640	~7
YH_2 [24,26]	Ti–1.5Fe–2.25Mo	0	–	~685	~634	~4.8
		0.6	–	~645	~553	~7.6
LaB_6 [22,26]	Ti–1.5Fe–2.25Mo	0	~93	~685	~634	~4.8
		0.15	~94	~759	~650	~7
		0.3	~93.8	~720	~645	~4
		0.6	~93.2	~700	~640	~3.8
		1.2	~91.8	~650	~580	~2.8
		3.0	~87	~640	~575	~2.5

UTS: ultimate tensile strength; YS: yield strength (0.2% offset).

metal powder (<100 μm) with Ti–6Al–4V alloy powder in argon and consolidated the powder mixtures by a laser rapid forming (LRF) process. The tensile elongation increased from ~4% to ~9% with an addition of 0.2 wt% Nd but dropped beyond that. Nevertheless, it is not very practical to introduce pure RE elements to PM Ti. Recently, Liu et al. [38–41] introduced RE elements to PM Ti alloys in various forms, including RE boride (LaB_6) powder or RE hydride (LaH_2, YH_2) powder etc., and achieved noticeably improved tensile ductility. Table 1 summarizes these efforts. Recent detailed studies of the addition of YH_2 powder to PM CP-Ti and Ti alloys revealed that YH_2 decomposed into pure yttrium (Y) and the scavenging of oxygen occurred through the formation of a range of oxygen-deficient Y_xO_y compounds with the same crystal structure as Y_2O_3 [42,43]. Also, the addition of YH_2 simultaneously scavenged chlorine (Cl) from the Ti powder leading to the formation of essentially oxygen-free binary Y–Cl compounds [42].

The use of Al–Nd master alloy powder is not suited to low Al content or Al-free PM Ti alloys. RE boride powder is a useful form of RE addition but the simultaneous introduction of B, even at a small amount (≤0.3 wt%), may offset the improvement in ductility. The use of RE hydride powder such as LaH_2 and YH_2 powder allows the introduction of pure RE elements to PM Ti alloys. However, they are not commercially available and are prone to oxidation when exposed to air. Hence, it would be useful to identify a different form of RE addition.

Cerium silicide ($CeSi_2$) appears to be one such promising candidate: (i) it is commercially available and also stable at room temperature; (ii) it is more affordable (USD $4.52/g) than other forms of RE compounds (USD $6.7/g for LaB_6, USD $7.02/g for $LaSi_2$) [44]; (iii) compared to B, Si has a good solubility in α-Ti. This permits a high level of RE addition for significant scavenging of oxygen without forming brittle silicides; and (iv) a small addition of Si (0.5 wt%) is effective in enhancing the densification and strengthening of PM Ti alloys [45,46]. To date, no information exists about the use of $CeSi_2$ in PM Ti alloys. It is unknown if $CeSi_2$ will be able to scavenge oxygen and chlorine from the Ti powder and how the mechanical properties will respond accordingly.

This paper investigates the effect of a small addition of $CeSi_2$ on the impurity scavenging, sintering densification, microstructure and mechanical properties of PM CP-Ti (Grade 2), Ti–6Al–4V and Ti–10V–2Fe–3Al. These three Ti materials are selected because of their commercial importance and their established microstructure–property relationships in the as-sintered state by the cold-compaction-and-sinter process.

2. Experimental procedure

HDH Ti powder (99.5% purity, 0.25%O, 0.05%Cl, −250 mesh), supplied by Kimet, China, and two master alloy powders, 66.7V–13.3Fe–20Al (in wt%, 99.5% purity, −325 mesh) and 58V–42Al (in wt%, 99.5% purity, −325 mesh), supplied by Baoji Jia Cheng Rare Metal Materials Co. Ltd., China, were used. Aluminum powder (99.7% purity, ~3 μm), supplied by Aluminum Powder Company Ltd., UK, was used to balance the composition of Ti–6Al–4V alloy due to the use of the 58V–42Al master alloy powder. A small ingot of $CeSi_2$ (99.5% purity) supplied by Alfa Aesar was crushed into powder by manual grinding for 2 min in a mortar at room temperature. To distinguish between the roles of Ce and Si introduced as $CeSi_2$ in sintering densification, the equivalent amount of elemental Si powders (≤45 μm, 99.5% purity, supplied by the CERAC Inc., USA) were introduced to the powder mixture of Ti–10V–2Fe–3Al alloy. The cold compaction process was similar to that described in a previous study [47]. Green tensile bars with dimensions of approximately 3.3 mm×3.5 mm cross-section and 18.6 mm gauge length (total length: 56.6 mm) were compacted at 600 MPa in a floating die specially designed for tensile testing. The as-sintered tensile samples measured about 3.25 mm×2.9 mm cross-section and 15 mm gauge length.