

Powder Metallurgy of Titanium at the 12th World Conference on Titanium

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马 前

Abstract: The 12th World Conference on Titanium has seen the presentation of a number of noteworthy developments that were aimed at achieving cost reductions and/or improved constitutional and microstructural capabilities through the conventional cold-compaction-and-sinter powder metallurgy (PM) approach. This review discusses several such developments, including the scavenging of oxygen and chlorine from Ti powder compacts during sintering by minor additions of rare earth compounds, the advantages of PM Ti fabrication with TiH₂ powder over elemental Ti powder, the efforts to develop ultrafine as-sintered microstructures from the use of TiH₂ powder, the design of sintering pathways for high solute content alloys such as Ti-10V-2Fe-3Al, and the positive implications of microwave-assisted sintering of commercially pure (CP) Ti and Ti alloys.

Key words: power metallurgy of titanium; cold-compaction-and-sinter; microwave-assisted sintering

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钛粉末冶金研究进展

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摘 要: 从第12届世界钛会可以看出, 传统钛粉末冶金即冷压烧结在降低钛制品的制造成本和改进烧结钛制品的成分及显微组织方面已有了许多可喜的进展。结合第12届世界钛会有关钛粉末冶金方面的研究报告, 主要从钛粉体烧结过程中氧和残留氯化物的去除和控制、使用氢化钛粉的优点、通过控制氢化钛粉烧结过程相变制备出具有超细(亚微米至几个微米)显微组织特征的高性能钛材料、合金元素含量高钛合金的烧结特点、微波辐射烧结钛及钛合金几个方面讨论了钛粉末冶金相关研究的最新进展。

关键词: 钛粉末冶金; 冷压烧结; 微波辐射烧结

1 Introduction

The first major effort documented to fabricate Ti alloys from powder was made by Kroll^[1]. The magnesium reduction approach initiated by Kroll allowed him to be able to produce ~ 0.5 kg batches of Ti powder or sponge fines in 1937^[2-3]. Kroll subsequently compacted and sintered 14 binary Ti alloys (Mo, W, Ni, Fe, Co, Be, Si, Mn, Cr, Cu, Al, Zr, V and Ta) in argon, with additions ranging from 2% to 9%. The sintered samples (ϕ 19 mm diameter cylinders) were then hot-rolled into strips of ~ 1 mm thickness for ductility assessment^[4]. Over the last 74 years, particularly since

the early 1950s following the commercial production of Ti sponge in the United States (in 1948), the UK (in 1951), Japan (in 1952) and the former USSR (in 1954)^[1], both blended elemental (BE) and pre-alloyed (PA) PM approaches have been investigated as cost-effective techniques for the production of near-net or net shaped CP Ti and Ti alloy products^[5]. Although wrought grade properties are achievable, the potential of the PM route is yet to be realised as a significant industrial approach for CP Ti and Ti alloys. Current tonnage applications are limited to just a few products, most notably the PM-based Ti engine valves for YAMAHA motorcycles and Toyota sporting cars^[1], and titanium filtration tubes up to a few hundred millimetres in diameter, sintered from elemental Ti powder. Despite the slow pick-up in the market, researchers have worked relentlessly to improve the technical capabilities of various PM Ti processes. This paper discusses the highlights from several presentations at

the 12th World Conference on Titanium focusing on the conventional cold-compaction-and-sinter PM process. The conventional PM process is technically the simplest and economically the most attractive near-net shape or preform PM fabrication approach, suited to non-fatigue-critical applications.

2 Scavenging of oxygen and chlorine

The ductility of CP Ti and Ti alloys is sensitive to their oxygen contents. The ability to mitigate the detrimental effect of oxygen on ductility holds the key to the development of many cost-effective ductile PM Ti products and/or preforms by either the conventional PM process or the more recently developed titanium injection moulding process. Liu and co-workers^[6] of Central South University, China, discussed the use of yttrium (Y) to mitigate the effect of oxygen. A Ti-1.5Fe-2.25Mo-0.6Y (all in mass fraction) alloy was sintered from elemental powder blends of Ti, Fe, and Mo with Y being introduced as YH₂ powder (< 74 μm). The addition of 0.6% Y increased the ductility of the as-sintered alloy from 4% to 7.6% and the ductility of the forged and annealed alloy (from as-sintered preform) from 14.8% to 22%. X-ray diffraction (XRD) revealed the existence of Y₂O₃ in the forged and annealed alloy (see Fig. 1^[6]), indicative of the effective oxygen scavenging role of Y. The Y₂O₃ particles were shown to align with the deformation direction in the as-forged microstructure; they were also visible on the fractured surfaces. The work presented confirmed that rare earth elements have the potential to be a potent scavenger for oxygen in titanium due to their higher affinity for oxygen.

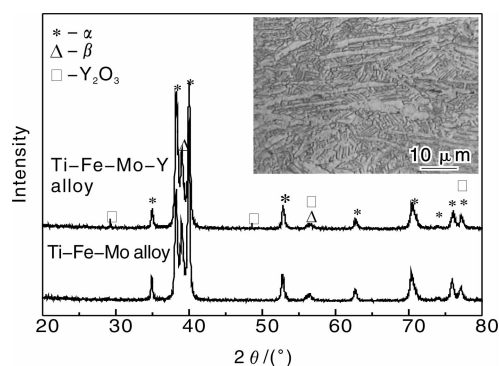


Fig. 1 XRD spectra of forged and annealed Ti-1.5Fe-2.25Mo and Ti-1.5Fe-2.25Mo-0.6Y alloys from as-sintered preforms made from elemental powder blends of Ti, Fe, and Mo with Y being introduced as YH₂ powder (< 74 μm). The inset shows the optical microstructure of the forged and annealed Ti-1.5Fe-2.25Mo-0.6Y alloy. The Y₂O₃ phase was detected in the Ti-1.5Fe-2.25Mo-0.6Y alloy

The chloride impurities in Ti powder are another potential barrier to the manufacture of cost-affordable high performance PM Ti products. Titanium metal is currently produced mainly by the Kroll process, which involves thermo-chemical reduction of titanium tetrachloride by molten magnesium. The volatile behaviour of chlorides at high temperature causes macroporosity during sintering which impairs mechanical properties^[7]. In addition, the presence of chlorides causes unexpected problems during welding. This was first experi-

enced by DuPont, which initiated a near-net-shape PM route to mill products in the 1950s, with a view to achieving cost reduction by bypassing the Ti melting operations. DuPont stopped the development in 1962 because the residual chlorides in the mill products originating from the Ti powder were found to volatilise rapidly during fusion welding, leading to an unexpected build-up on the welding electrode that resulted in inconsistent weld quality^[1,8]. To avoid this issue, the chlorine content needs to be < 50 × 10⁻⁶, which was judged at that time to be impractical or too costly by DuPont. Mitigation efforts have been ineffective^[7].

Low and co-workers^[9] of The University of Queensland, Australia, reported their recent finding of scavenging chlorides from Ti powder with minor additions of rare earth (RE) compounds such as Y₂O₃, Nd₂O₃, and Er₂O₃. Point and mapping analyses of the RE₂O₃ oxide particles in the as-sintered microstructure by energy-dispersive X-ray spectroscopy (EDX) revealed clear evidence of the RE oxides absorbing chlorine from the Ti matrix. The scavenging resulted in a dramatic improvement in the sintered density of selected Ti alloys.

Although the actual impact of this finding on PM Ti alloy development and fabrication remains to be tested, including a necessary clarification of the influence of the oxide particles introduced, it demonstrates that the chloride impurities in Ti powder can be scavenged effectively this way. It appears that both oxygen and chlorine can be scavenged by minor additions of the same additive, yttrium (Y), where oxygen scavenging may occur first leading to the formation of Y₂O₃, which then scavenges chlorine, or the scavenging of oxygen and chlorine may occur simultaneously.

3 Advances in the use of TiH₂ powder

Savvakini et al.^[10] of Insitufe for Metal Physics, Ukraine, discussed the use of TiH₂ powder in comparison with the hydrogenated-and-dehydrogenated (HDH) elemental Ti powder.

Titanium hydride is brittle; it has a low strength (150 ~ 250 MPa) and poor plasticity (< 3%) under compression^[10]. Hence, TiH₂ particles fragment easily during compaction leading to much smaller sizes^[10]. When heated in vacuum at 7 °C/min, dehydrogenation starts from ~ 320 °C and develops vigorously in the range of 400 ~ 600 °C due to the formation of the β-Ti phase in which the hydrogen diffusivity is improved. Dehydrogenation finishes at ~ 800 °C^[10]. The phase transformation occurs in the sequence of TiH₂ → β → α, determined by in situ X-ray analysis^[10]. Powder compacts of TiH₂ show greater shrinkage than those of HDH Ti because of the volume changes upon dehydrogenation^[10]. In addition, Ti products sintered from the TiH₂ powder show lower oxygen contents than those sintered from the HDH Ti powder. The emission of H₂O during hydrogen evolution was detected by mass spectrometry. It was proposed that when leaving a TiH₂ powder particle hydrogen reduces the surface oxide layer prior to the oxide dissolving into the Ti metal^[10], where the dissolution of oxide occurs from ~ 700 °C^[11]. This decreases the oxygen content in the dehydrogenated titanium.

Encouraging mechanical properties are obtained from

sintering TiH_2 powder (3.5% H (mass fraction), $< 100 \mu\text{m}$, mean particle size: $40 \mu\text{m}$) for CP-Ti and Ti alloys (see Table 1^[10]). As an indication, Fig. 2 highlights the difference between the microstructures of Ti-6Al-4V sintered from TiH_2 powder (Fig. 2a) and HDH Ti powder (Fig. 2b)^[11].

Table 1 Properties of CP Ti and Ti alloys sintered from TiH_2 powder (3.5% H (mass fraction), $< 100 \mu\text{m}$, mean particle size: $40 \mu\text{m}$) at 1 250 °C

Alloy	Relative density /%	Grain size/ μm	YS /MPa	UTS /MPa	El. /%
CP-Ti	98.5	180	490	562	21
Ti-6Al-4V	98.1	82	885	975	12
Ti-5553	97.3	75	966	1 064	10
Ti-1023	96	105	944	1 033	8
Ti-1023 *	98	82	1 115	1 250	5.2

* fast heating rate, sintering at 1 200 °C

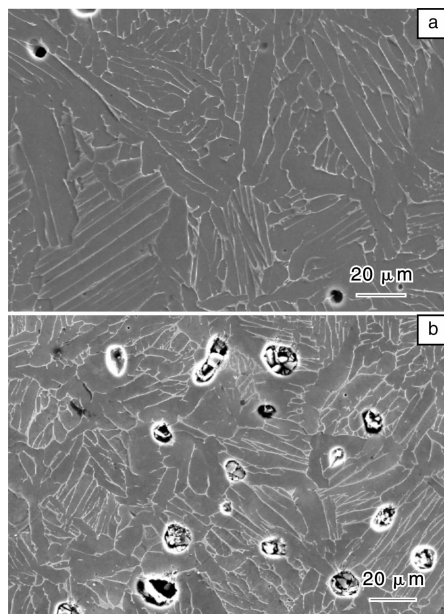


Fig. 2 Ti-6Al-4V sintered from (a) TiH_2 powder and (b) HDH Ti powder at 1 200 °C for 4 h. Relative densities: (a) 98.9% and (b) 96.3%

Fang and co-workers^[11] of University of Utah, USA, presented their efforts to develop ultrafine grained Ti materials from sintering TiH_2 powder through control of the phase transformations during sintering. Microstructural features from sub-micrometers to a few micrometers are produced in the as-sintered microstructure of Ti-6Al-4V, distinguishing from the microstructure of Ti-6Al-4V reported previously. The properties of the Ti-6Al-4V sintered this way attained UTS = 1 036 MPa, YS = 943 MPa, and tensile elongation = 15% with a relative density of ~99%. These properties are very encouraging. A US patent of the new development is pending^[11].

4 Sintering of high solute content alloys

The presentation by Qian and co-workers^[12] of The Uni-

versity of Queensland, Australia, discussed in detail the sintering of Ti-10V-2Fe-3Al compacted from HDH Ti powder (~100 mesh, 99.5% purity) with two different master alloy powder products, a ternary 66.7V-13.3Fe-20Al (99.5% purity), equivalent to 10V-2Fe-3Al, and a binary 85V-15Al (99.5% purity). The apparent activation energy for sintering, determined from the dilatometry data, is shown in Fig. 3^[12-13] with respect to the use of the two master alloys.

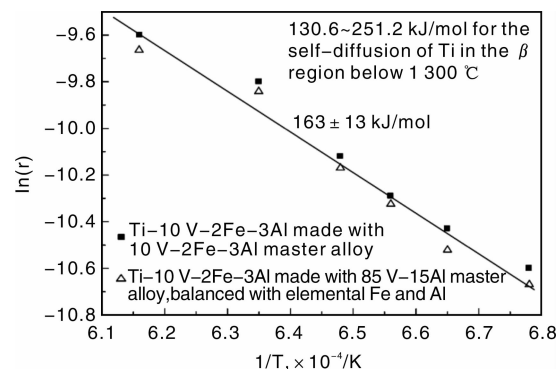


Fig. 3 Logarithmic shrinkage rate $\ln(r)$ versus $1/T$ for the sintering of Ti-10V-2Fe-3Al compacted from HDH Ti powder ($75 \sim 145 \mu\text{m}$) and master alloy powder ($48 \sim 75 \mu\text{m}$) blends at 400 MPa (heating rate: $5 \text{ } ^\circ\text{C}/\text{min}$)

The apparent activation energy obtained, $163 \pm 13 \text{ kJ/mol}$, falls into the activation energy range ($130.6 \sim 251.2 \text{ kJ/mol}$) for the self-diffusion of Ti in the temperature range $898 \sim 1\,540 \text{ } ^\circ\text{C}$ ^[14]. This indicates that the sintering of Ti-10V-2Fe-3Al is essentially controlled by the self-diffusion of Ti, which appears to be little affected by the presence of other diffusers, including the 10% V. However, the microstructure was shown to be strongly dictated by the diffusion of V. As a result, the use of the 10V-2Fe-3Al master alloy powder resulted in the development of a microstructure consisting of largely uniform α and β colonies while the use of the 85V-15Al master alloy powder led to a very non-uniform microstructure with acicular α precipitates at most grain boundaries. Consequently, the use of the 10V-2Fe-3Al master alloy produced much better ductility ($8.2 \pm 0.8\%$) than the use of the 85V-15Al master alloy ($3.3 \pm 1.2\%$; 0.53% O (mass fraction)) at similar sintered densities ($98.7 \pm 0.3\%$ vs $98.5 \pm 0.4\%$) and oxygen contents (0.50% vs 0.53% (mass fraction)). However, prolonged isothermal sintering resulted in similar properties from the 85V-15Al master alloy.

The authors concluded that the challenge for the fabrication of high solute content alloys such as Ti-10V-2Fe-3Al from powder is not densification, which is trivial with relatively fine Ti powder. Rather, it is the realisation of a desired microstructure through master alloy selection or design of the sintering pathway, which determines the distribution of the principal alloying element V, a slow diffuser in β -Ti. This distinguishes the sintering of Ti-10V-2Fe-3Al from the sintering of CP-Ti and lean Ti alloys, where the focus has predominantly been on densification. More details can be found from Ref. [13].

5 Microwave-assisted sintering of CP Ti and Ti alloys

Titanium is a paramagnetic metal which couples weakly with microwaves. Luo and co-workers of The University of Queensland, Australia discussed the sintering characteristics of CP-Ti, Ti-6Al-4V and Ti-10V-2Fe-3Al by microwave (MW) radiation in their presentation. The samples were sintered in a 3 kW, 2.45 GHz multi-mode high-vacuum (10^{-3} Pa) MW system, with the assistance of MW susceptors. Controllable heating up to 50 °C/min in vacuum was readily achievable by MW radiation, in contrast to the much slower heating by conventional vacuum sintering. Fig. 4 illustrates the sintering cycles achieved by MW radiation and conventional vacuum sintering. More details are available from Ref. [15]. The work presented suggests that the intrinsic weak response of Ti to MW radiation can be effectively mitigated by using MW susceptors. This may be attractive for the fabrication of some small PM Ti parts.

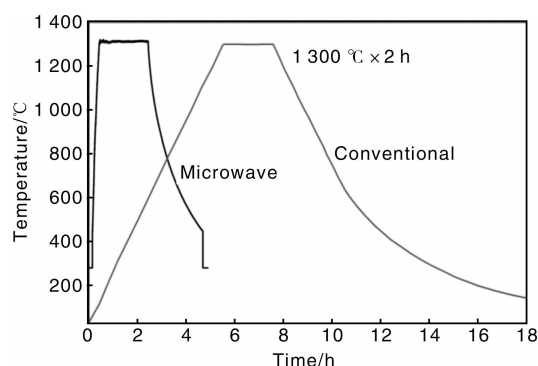


Fig. 4 Comparison of microwave and conventional vacuum sintering cycles

6 Concluding remarks

This review focused on presentations that are relevant to the conventional cold-compaction-and-sinter PM approach. These include the scavenging of oxygen and chlorine from Ti powder by minor additions of rare earth compounds, the advances in PM Ti fabrication with the use of TiH₂ powder, the efforts to develop ultrafine as-sintered microstructures based on the use of TiH₂ powder, the improved fundamental understanding of the sintering of high solute content alloys such Ti-10V-2Fe-3Al, and the positive implications demonstrated by the microwave-assisted sintering of CP Ti and Ti alloys. These developments are expected to

lead to more encouraging developments in PM Ti in the near future.

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