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The chemical state and control of oxygen in powder metallurgy tantalum

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ABSTRACT

Tantalum powders containing different oxygen concentrations have been vacuum hot-pressed in graphite dies to study the dissolution and precipitation of oxygen and carbon in powder metallurgy (PM) tantalum. Various types of oxide and carbide precipitates were observed using microscopy and analyzed by X-ray microdiffraction. An in situ contact gettering method using zirconium has been coupled with hot-pressing to control oxygen. This method is effective at removing oxygen from the solid solution, while the precipitation behavior is not significantly altered. Hardness profiles with distance from Zr contact agree well with those expected from oxygen concentration profiles predicted by analysis assuming a diffusion-limited rate of gettering. Corresponding lattice parameter measurements by microdiffraction indicate that oxygen prefers to stay in supersaturated solid solution, even under slow cooling, where it is much more effective in hardening than in the form of precipitates.

1. Introduction

With the current state-of-the-art melting practices, very low interstitial impurity levels can be achieved in as-cast tantalum, typically (in weight ppm): oxygen < 50, nitrogen < 25, carbon < 10 and hydrogen < 1 [1]. However, banded microstructures exhibiting a mixture of recrystallized and unrecrystallized grains, highly variable grain sizes and rolling texture gradients associated with deformed and annealed ingots of cast tantalum [1–4] make the mechanical properties non-uniform and unpredictable. Powder metallurgy (PM) methods such as hot isostatic pressing, spark plasma sintering (SPS) and hot-pressing have been employed in order to produce more uniform and consistent mechanical properties [5–7]. PM tantalum components are relatively texture free and can perform better than cast and forged plates in certain applications [6–8]. However, the high affinity of tantalum for interstitials presents serious problems in powder metallurgy, where large surface area powders are exposed to these elements in powder production and consolidation at high temperatures. Although PM is still very attractive for certain tantalum applications, high interstitial contents typically limit formability and ductility compared to the ingot metallurgy tantalum.

Oxygen has been the most important problem in PM tantalum and the most studied over the past few decades. Oxygen dramatically increases the hardness of tantalum [9,10], but there has been a debate in the literature about its effect on ductility. Some researchers claimed that increasing oxygen content has no or little effect on the ductility [5,11–13], while others showed detrimental effects [14–16]. A possible reason for these disagreements is that oxygen can exist in two chemical states in tantalum, in solid solution and as oxide precipitates. Studies on wrought tantalum by Gebhardt and Preisandanz [14] and Ingram et al. [15] clearly showed how oxygen can be detrimental for ductility, especially concentrations higher than 500 wt. ppm. However, the chemical state of the oxygen was not mentioned in either of these studies. Previous work detailed below has shown that at high concentrations, the chemical state of oxygen in tantalum depends strongly on the processing temperature and cooling rate. Therefore, controlling the chemical state of oxygen in tantalum may be as important as its concentration in PM applications. Yet, the open literature is lacking definitive microstructural studies on oxygen effects in PM tantalum.

The present study provides new insights on the chemical state and control of oxygen in PM tantalum through controlled-oxygen hot-pressing experiments. Blending of lower oxygen powders produced from machining chips with higher oxygen commercial capacitor powders enabled systematic variations in the concentration and chemical state of oxygen. The resulting microstructures and microhardness are characterized in detail and compared with thermodynamics and kinetics predictions. An in situ oxygen gettering method is demonstrated to resolve the oxygen problem of this PM method. Coupled with the gettering study, the chemical state of the oxygen and the corresponding effects on microhardness are correlated to address the findings in the previous literature.

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2. State of oxygen in tantalum and effects on hardness

The solubility of oxygen in Ta in equilibrium with Ta_2O_5 is well established, increasing approximately linearly from ~1 at.% (900 wt. ppm) at 500 °C to 4.9 at.% (4500 wt. ppm) at 1550 °C [8,17]. Supersaturated solid solutions form readily, however, as the precipitation of Ta_2O_5 is sluggish, possibly due to the low homologous temperatures in this range. Therefore, some equilibrium solubilities published in the literature may not be valid and may reflect supersaturated solutions resulting from non-equilibrium cooling [8,10].

Stecura [10] and Hörz [9] showed that the room-temperature lattice parameter and hardness of Ta increase nearly linearly with increasing oxygen in solid solution. Starting with Ta of greater than 99.95 wt.% total purity, Stecura [10] measured the hardness to increase from ~120 HV for undoped specimens (containing 0.05–0.1 at.% total interstitials) to ~500 HV at 2.4 at.% oxygen. Hörz [9] employed higher purity Ta and high temperature vacuum degassing to produce undoped specimens containing less than 0.003 at.% total interstitials. The undoped specimens exhibited a hardness of 80 HV, increasing to 550 HV at 4 at.% oxygen in supersaturated solution. More recent studies on low-interstitial, triple electron-beam melted and annealed Ta indicate hardness value of ~87 HV, with a grain size of 42 μm [18].

Hörz studied the precipitation of oxides from supersaturated Ta–O solid solutions containing 1–4 at.% oxygen at temperatures from 423 to 1173 K [9]. Aging at 423 and 473 K resulted in mild precipitation hardening, with a peak hardness increase of ~20%, due to the formation of metastable, coherent tantalum suboxides. At higher aging temperatures (873–1173 K), however, the initial solid solution hardness decreased continuously as the oxygen in solid solution was depleted by precipitation of the stable and incoherent Ta_2O_5, plateauing to values corresponding to the hardness of the saturated solution, which decrease with decreasing aging temperature [9]. These results show that the hardness of Ta–O alloys is governed by the oxygen in solid solution, with Ta_2O_5 precipitates contributing essentially no hardening due to their incoherency and low concentration [9,16,19,20]. These results provide a basis for analyzing the present study on the state of oxygen in PM Ta.

The present work originated from a study of tantalum powder production via machining. By starting with wrought Ta having low oxygen content, oxygen contamination is limited to that from new surface formation. The larger size and lack of porosity of the chip particles also provides an advantage through lower surface area-to-volume ratio compared to the conventional metallurgical or capacitor grade powders and ultrafine (or nano) size particles, without the high external surface area and associated challenges of severe contamination and agglomeration in consolidation [21,22]. In addition, severe plastic deformation in chip formation leads to grain refinement within the particles, providing a route to study the recrystallization behavior with respect to the oxygen content and the chemical state [23,24]. Thus, the machining chip powders provided a unique framework for systematic studies on the role of oxygen in microstructure development in PM tantalum.

3. Experimental procedures

3.1. Powder production and characterization

The machining chip powders were produced by Nanodynamics Inc. (NDI), Buffalo, NY. Chips (50–5000 μm) milled from commercially pure tantalum plate (min. 99.90 wt.% Ta, Rembar Inc., Dobbs Ferry, NY) showed a hardness increase from 90 ± 20 kgf/mm^2 (plate) to 267 ± 15 kgf/mm^2 (chips), indicating the effect of severe plastic deformation. Optical micrographs (Fig. 1) show the regular shape of the chip particles and extensive flow lines indicative of ultrafine grain formation [23,25,26]. EBSD analysis confirmed the average grain size of the machining chips was ~200 nm, compared to 120 μm in the starting wrought plate. The grain size and corresponding hardness are in good agreement with the results of Mathaudhu and Hartwig [27].

The powders were analyzed for oxygen content by inert gas fusion-absorbance and nitrogen content by inert gas fusion-thermal conductivity (IMR Test Labs, Lansing, NY). Oxygen contents of the starting plate and resulting chips were measured to be 100 wt. ppm and 230 wt. ppm, respectively. Raw chips were then either chopped in a hammer mill in air (chopped) or jet-milled in air (Air JM) or nitrogen atmosphere (Nitrogen JM). Results in Table 1 show how milling atmosphere changes the oxygen content of the chip powders significantly and the milling in a nitrogen atmosphere reduced, but did not eliminate, oxygen contamination. The results also show that oxygen contamination decreases with increasing particle size, consistent with the corresponding lower surface area. Nitrogen content measured for all powders, chips and starting material ranged from 10 to 50 wt. ppm, depending on the particle size distribution. Tap densities of the powders are also given in Table 1.

3.2. Hot-pressing

Hot-pressing was conducted at 1100–1500 °C under vacuum (600–1000 mTorr) in cylindrical graphite dies (26 or 63-mm diameter) in a 30-ton Elatec Pressvac™ series uni-axial vertical hot-press. The heating elements were also graphite and temperatures were measured by a thermocouple and an optical pyrometer. Die walls were lined with GTB grade, 0.4 mm-thick Ucar Grafoil® (Union Carbide) graphite foil to prevent reaction between the powder and die surfaces. A heating rate of 10 °C/min was used for all runs. All

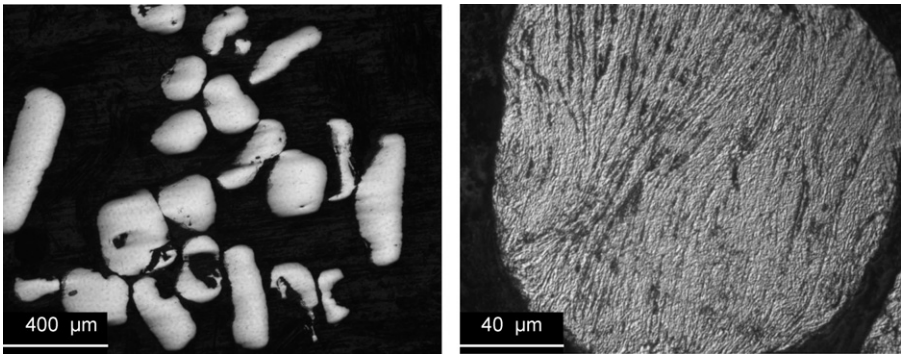

Fig. 1. Particle shape and optical microstructures of 150–250 μm nitrogen jet-milled NDI powders. Left (unetched) showing size distribution and right (etched) showing deformation bands indicative of ultrafine grained microstructure.