DEEP CRYOGENIC TREATMENT OF TITANIUM-BASED ALLOYS

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ABSTRACT

Deep cryogenic treatment (DCT) involves cooling materials to extremely low temperatures, for extended isothermal holds, to modify physical properties in a positive manner. DCT has been successfully applied to a variety of ferrous alloys, invariably enhancing hardness and wear properties. In contrast, only limited studies have been conducted applying DCT to titanium alloys. In the present work, DCT has been used to treat both commercially-pure Ti (CP-Ti) and an aerospace-grade α-/β-Ti alloy (Ti-6Al-4V). The DCT process steps involved cooling the Ti alloys to -196 °C, and then holding at this temperature for a fixed period of time (10, 24, or 72 hours), before returning to room temperature. Treated samples were investigated in terms of their microstructures, mechanical behaviour, and aqueous corrosion resistance (in 3.5 wt.% NaCl solution). DCT yields subtle changes in microstructure and tensile properties for both alloys. Measurable improvements in corrosion resistance were noted, especially for the shorter duration DCT schedules (10 or 24 hours). It is demonstrated that DCT can provide beneficial effects when used for Ti-based systems.

KEYWORDS

Commercially pure titanium, Corrosion testing, SEM, Tensile behaviour, Ti-6Al-4V, Vickers hardness

INTRODUCTION

Titanium (Ti) is a used in many engineering applications due to a high strength to weight ratio, low thermal conductivity, strength retention at high temperatures, and exceptional corrosion resistance (Collins, 1989). There are many methods that attempt to improve selected properties in titanium alloys, including peening and a variety of heat treatments. Deep cryogenic treatment (DCT) is a type of thermal ‘annealing’ procedure, only in this instance by cooling to cryogenic temperatures (and soaking at such temperatures) in a controlled manner. Pieces undergoing DCT are typically cooled to -196 °C, and then returned to ambient temperature, after which they may be further heat-treated. This process has previously been used to improve the mechanical properties of various metals, including steels. To-date, only limited application of DCT has been applied to Ti alloys, with mixed results (Gu et al., 2013; Gu, Wang, & Zhou, 2014). The current research examines DCT on two common Ti alloys, to ascertain the efficacy of this approach for industrial applications.

EXPERIMENTAL

Two Ti alloy grades are used in the present work; commercially pure Ti (CP-Ti) and Ti with 6 wt.% Al and 4 wt.% V additions (Ti-6Al-4V); Ti-6Al-4V is a dual-phase α-/β- titanium alloy. Four groups were evaluated for each alloy: No DCT, 10 h DCT, 24 h DCT, and 72 h DCT. Before each of the Ti alloy samples underwent their cryogenic treatment, they were annealed in Ar (CP-Ti: 2 h/700 °C, Ti-6Al-4V: 2 h/ 760 °C). Samples were cooled to -196 °C with liquid nitrogen, at a rate of 1 °C/minute, then held at -196 °C for the required test time (10, 24, or 72 h), then returned to room temperature (approximately 20 °C).

Polished samples were etched with Kroll's solution for ~10 seconds to show the different structures. Microstructures of as-received and DCT samples were analysed using scanning electron microscopy (SEM). X-ray diffraction (XRD) was used for crystal structure determination. Vickers hardness (1 Kgf) and tensile tests were performed on all samples. 'Buttonhead' tensile samples were used, threaded at both ends, with a gauge diameter of 6 mm and gauge length of 25 mm, generally following ASTM E8/ E8M-21 for tensile testing of metallic materials. All tests were conducted at room temperature. Four samples were tested for each alloy and treatment condition. Electrochemical measurements were carried out following the ASTM standard G59-97 potentiodynamic polarisation test method. Corrosion tests were conducted in a three-electrode flat cell, with the sample as the working electrode (1 cm^2 area), a platinum mesh (Pt) as the counter electrode, and a saturated calomel electrode (SCE; −0.241 V vs. a standard hydrogen electrode) as the reference. The electrolyte was prepared using 3.5 wt.% NaCl in distilled water.

RESULTS

Figure 1 shows SEM images comparing the as-received Ti-6Al-4V alloy with the same material DCT processed for 24 hours. DCT slightly increases the concentration of β-Ti grains within the α-Ti matrix of the Ti-6Al-4V alloy with increasing duration, and the size of individual grains also appears slightly larger. Similarly, subtle changes were also noted for the CP-Ti after DCT processing. XRD analysis also confirmed that there are only very minor changes to the microstructure. These changes are small, and as such it is difficult to suggest that any improvement in properties could result from these slight changes in composition.

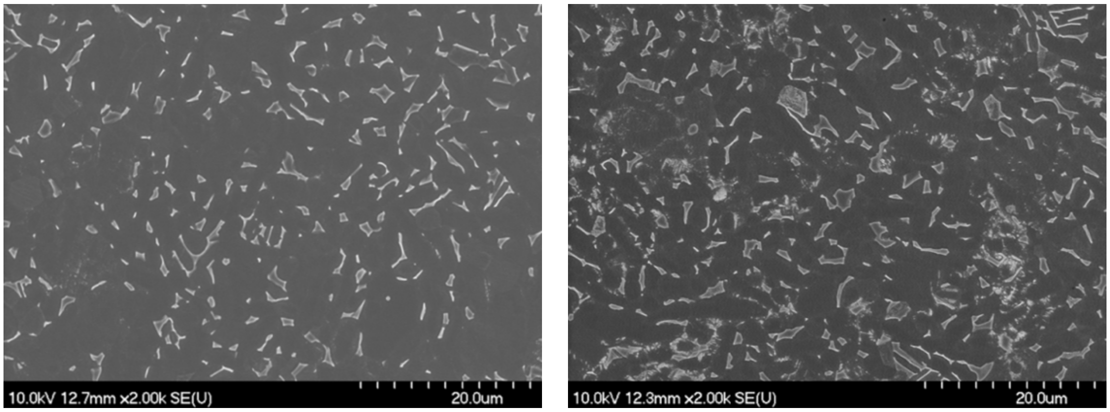

Figure 1. Representative SEM microstructural images of Ti-6Al-4V: (a) as-received, and (b) 24 h DCT.

The Vickers hardness values of both CP-Ti and Ti-6Al-4V do not change significantly with DCT. Previously published data in the literature relating to DCT of Ti-6Al-4V yielded similarly minimal differences in Vickers hardness (Gu et al., 2013; Gu et al., 2014), which is largely confirmed in the current study. Tensile test data is summarised for DCT of CP-Ti in Table 1 and Ti-6Al-4V in Table 2. Some slight trends are apparent in the tensile data. The Young's modulus of CP-Ti increases, then decreases, with increasing DCT soak time, although a similar trend is not observed in Ti-6Al-4V. The CP-Ti ultimate tensile strength shows no clear trend, while Ti-6Al-4V shows an increasing then decreasing strength as soaking time increases. There are no clear trends in yield strength over the various soak times for either alloy. The CP-Ti ductility shows a slight increase then decrease with DCT soak time, while TI-6Al-4V shows no clear trend. In each case, observations are fairly subtle, and do not show the benefits that are more typically apparent with ferrous alloys (Tyshchenko et al., 2010; Vahdat, Nategh, & Mirdamadi, 2013; Li et al., 2016). The difference between the largest and smallest values for the CP-Ti Young's modulus is less than 4 GPa, and between Ti-6Al-4V ultimate tensile strength is less than 5 MPa, for an absolute increase of 3.7% and 0.46% respectively.

The open circuit potential (OCP) typically showed an increase to more positive values, regardless of the composition, with the exception of Ti-6Al-4V treated with a 72 hour DCT soak duration. These observations indicate that a short duration DCT process (*i.e.*, 10 hours) does result in an improvement in the corrosion resistance, especially for CP-Ti. Figure 2 presents the measured potentiodynamic polarisation curves obtained for the CP-Ti and Ti-6Al-4V samples, both untreated and after 10, 24 and 72 hours DCT in 3.5 wt.% NaCl solution. The polarisation curves for both alloys show a general improvement in the corrosion characteristics (*i.e.*, increase in E_{corr} and decrease in i_{corr}), with increasing of the DCT soak time up to 24 hours, in accordance with the OCP studies, confirming the benefits of DCT for Ti alloys.

Table 1. Average tensile test data for the CP-Ti samples

DCT Time (h)	Young's Modulus (GPa)	Ultimate Tensile Strength (MPa)	Yield Strength (MPa)	Maximum Elongation (%)
No DCT	104.9	499.8	371.6	24.9%
10	107.3	498.7	369.7	24.8%
24	108.5	498.0	368.0	25.1%
72	105.4	498.1	368.0	24.7%

Table 2. Average tensile test data for the Ti-6Al-4V samples

DCT Time (h)	Young's Modulus (GPa)	Ultimate Tensile Strength (MPa)	Yield Strength (MPa)	Maximum Elongation (%)
No DCT	105.0	1091.8	939.4	14.5%
10	103.3	1092.4	914.9	15.4%
24	105.4	1095.6	934.3	14.0%
72	105.7	1091.0	946.0	14.6%

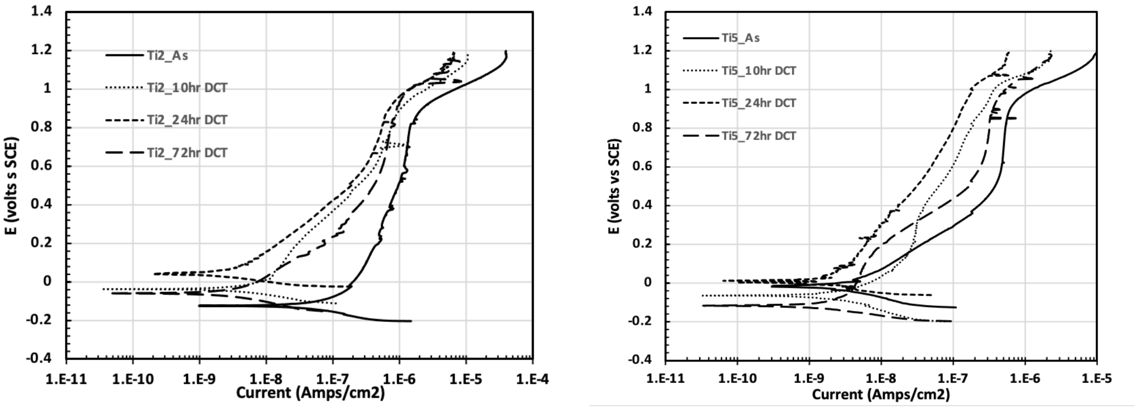

Figure 2. Potentiodynamic polarisation curves obtained following DCT for 10, 24 and 72 hours in 3.5 wt.% NaCl solution at 21 ± 2 °C for: (a) CP-Ti (Grade 2), and (b) Ti-6Al-V4 (Grade 5).

CONCLUSIONS

It is demonstrated that DCT has only minimal effect on either CP-Ti or Ti-6Al-4V in terms of their mechanical behaviour (hardness and tensile response). In contrast, the corrosion response of the alloys is demonstrably improved through DCT (*i.e.*, increases in OCP and E_{corr}, and decreases in i_{corr}), warranting further study of DCT for specific applications where corrosion resistance is needed (*e.g.*, biomedical).

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