Titanium Nitriding Methods: Drawbacks and Benefits

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The application of titanium alloys in aircraft construction is expanding due to their high corrosion resistance and excellent strength-to-weight ratio. However, if not specially treated, they are characterized by relatively low wear resistance [1 (https://doi.org/10.1016/j.wear.2019.203094.),2 (https://doi.org/10.1038/s41598-020-76360-3)], a significant limiting factor for their application. The surface treatment may improve this characteristic, and diffusion-saturation by nitrogen is the gold standard, and this section discusses the features, benefits, and shortcomings of the most common titanium nitriding methods.

Keywords: nitriding ; titanium alloys

1. Plasma Nitriding

Plasma nitriding methods typically provide high hardness and case depth to treated surfaces. Moreover, the process is known to smoothen the surface profile of the sample [3]. However, various sharp edges may be burnt or overheated due to a local increase in the surface temperature; nevertheless, plasma nitriding is widely used to enhance the wear resistance of titanium alloys and steels [3].

Taktak and Akbulut [4] investigated the wear resistance of the titanium alloy Ti-6-4, which was nitrided in a plasma medium after detonation explosive shock treatment (DEST). After nitriding at temperatures up to 900 °C for 12 h, a maximum top surface hardness of 2500 $HV_{0.05}$ was reported. This value is much higher than found in other studies reviewed in this section. The authors did not explain it, but they probably obtained a dense compound layer consisting only of TiN due to the high strain induced by DEST. The wear tests showed [4] that nitriding significantly increases the wear resistance of titanium alloys. The primary wear mechanism of WC-Co vs. nitrided Ti-64 was fatigue-assisted abrasive wear.

Pure titanium was plasma-nitrided in [5]. The high hardness (1000–1300 $HV_{0.1}$ due to the formation of super-hard ε-Ti_2N and δ-TiN phases) and relatively low thickness (5–15 microns) created an unwanted sevenfold difference in hardness between the diffusion layer and the substrate. The high hardness values in [4][5] may also be explained by the low load used for Vickers indentation. According to the authors of [5], plasma nitriding of pure Ti resulted in a significant reduction in COF.

Plasma nitriding of a Ti5Al4V2Mo alloy in a mixture of nitrogen and argon [6] for 3–4 h at temperatures 500–900 °C produced a relatively hard surface (600–800 $HV_{0.05}$). Thus, we can conclude that using argon and reduced pressure does not promote significant layer thickness and hardness. In other work [7], a Grade 2 titanium alloy was plasma-nitrided at 650–950 °C (with 50 °C increments) for 8 h. The maximum surface hardness (1550 $HV_{0.05}$) and layer thickness (about 55 µm) were reported for plasma nitriding at 950 °C. However, increasing the nitriding temperature above 850 °C reduces the wear resistance of the alloy.

Plasma nitriding using an N_2–NH_3 gas mixture at temperatures of 700 and 750 °C was studied by Shen and Wang [8]. According to the results provided, a 2.3 µm compound layer for NH_3 and a 6.5 µm compound layer for the N_2–NH_3 gaseous mixture was obtained, which is much less than that achieved at higher temperatures.

Plasma nitriding provides the greatest layer thickness and hardness when applied at temperatures above 850 °C. Low-temperature plasma nitriding does not lead to high thickness or hardness in the modified layers. Plasma nitriding is quite a complicated method. It requires sophisticated equipment [4][5][6] and cannot always be reproduced in common manufacturing conditions. It greatly improves corrosion resistance. The best wear resistance was reported in plasma-nitrided Ti alloys for specimens treated at a temperature range of 800–850 °C [7]. Increasing the temperature of plasma nitriding from 700 to 850 °C improves the wear resistance [7][8]. On the other hand, reducing the process temperature reduces the surface roughness [5] and the coefficient of friction, thus increasing the wear resistance [4][8]. Moreover, a low-temperature process can improve the corrosion resistance of an alloy by creating a protective barrier [9].

2. Laser-Assisted Nitriding

For titanium alloys, the novel plasma-enhanced pulsed-laser deposition system [10] allows one to obtain a relatively thin nitride layer (more than 100 nm over 1 h), which is not very effective. Compared with plasma nitriding, laser-assisted gas nitriding [11] requires much more power (1–5 kW vs. 400–650 W [5]) for processing. Moreover, the plasma nitriding method treats all the exposed surfaces, while laser-assisted methods affect only the scanned surfaces. However, they may be used for selectively treated areas and textured surfaces [12] or thermocycled coatings [13][14]. While laser nitriding involves surface remelting and requires precise control of the saturation parameters, it is also hard to process internal surfaces via this method (e.g., holes for the insertion of bronze landing gear bushings). Obtaining a thick coating is not always possible, but their effective production has been reported [15].

3. Gas-Blow Induction Heating Nitriding Method

Induction heating of a Ti64 alloy in a nitrogen atmosphere generates a nitrided layer in only a few minutes [16]. The best wear resistance of the alloy is observed when the treatment temperature is 900 °C, as both compound and diffusion layers are formed. Nevertheless, at this temperature, coarsening of the microstructure may be observed, which has an adverse effect on the alloy's mechanical properties. Moreover, the authors of [17] removed the compound layer and discovered that this improved the fatigue resistance while reducing the wear resistance.

Low temperatures (650 °C) during gas-blow induction heating nitriding after shot peening with fine particles produce both diffusion and compound layers in a relatively short exposure time. The hardness of treated Ti-64 specimens is 400–450 $HV_{0.025}$, which is low. However, the highest substrate temperature can be observed not on the top of the sample but in the sublayer because the surface is cooled by gas flow during the induction heating process [18][19]. The gas-blow induction heating nitriding process has potential as a rapid nitriding technology, but it should be studied much more thoroughly than it has been to date.

4. Electron-Beam Vacuum Nitriding

This newly introduced method [20][21] uses an electron beam for nitriding under low (8–10 Pa) pressure. Pure titanium was used to manufacture the test specimens, and the results were quite positive. The strengthened layer thickness was 15–35 µm, and the surface micro hardness measured by the Vickers method at a load of 0.1 kg was up to 12 GPa (≈1200 $HV_{0.1}$). Though this technology may have a future as a type of plasma nitriding, it is necessary to develop it further for aerospace applications.

5. Gas Nitriding

Gas nitriding is probably the simplest of all nitriding methods. It requires only a furnace under good pressure control at the specified temperature ranges. The dynamic gas flow allows internal surfaces to be treated with the same efficiency as flat specimens. The nonoxidizing atmosphere during gas nitriding allows the heat treatment of the alloy in one step with thermochemical processing [23][24].

Gas nitriding was used to study the strengthening of the newly developed TZ20 (Ti-19.2Zr-6.48Al-3.86V-Hf-Na) alloy [25]. Increasing the temperature from 500 to 650 °C increased the weight gain from 0.62 to 3.67 mg/cm^2 (592%). The duration of the process was 260 min, and the nitrogen pressure in the reaction chamber was 0.05 MPa. The nitrided layer's thickness was 1–7 µm after 1 h, and the maximum value was 12–14 µm. The surface hardness increased from 470 $HV_{0.01}$ to 870 $HV_{0.01}$. In another study [26], intermittent vacuum nitriding of a TB8 (Ti-15.32Mo-3.23Al-2.86Nb) alloy at 780 °C gave much better results: a hardness of 850–900 $HV_{0.1}$ and a nitride layer thickness of up to 120 µm. We may conclude that an increase in temperature and nitrogen gas pressure results in a thicker compound layer and higher hardness, but this also strongly depends on the alloy's composition. The influence of higher temperatures under atmospheric pressure is presented in [27]: increasing the temperature and exposure time resulted in thicker and harder surfaces. A method of gas nitriding in an ammonia medium also produced good results [8][28]: at 1100 °C and atmospheric pressure, the layer's thickness was 40–50 µm after 5 h.

Gas nitriding is not effective for β-titanium alloys but is good for double-phase alloys in the region of the β-transus temperature [29]. Vacuum preheating has a beneficial effect on the gas nitriding process [30]. This helps to remove oxygen and other gaseous impurities from the surface and facilitates the thermal diffusion process. Regarding the BT22 titanium alloy, the standard heat treatment combines diffusion annealing [31] from the betta region (750–850 °C) and slow cooling.

This results in a uniform microstructure with a good combination of mechanical properties. High strength (up to UTS 1400 MPa) may be obtained after aging. This alloy may be used both in annealed and aged conditions.

Based on this analysis of nitriding's effects on the surface layer's properties [4][5][6][7][8][9][10][11][13][14][15][16][17][18][19][20][21][25][26][27][28][29][30][32], we decided to study gas nitriding of the double-phase high-strength BT22 titanium alloy. As higher temperatures and gas pressure results in thicker and harder surfaces, the process parameters selected are an atmospheric nitrogen pressure and temperature range of 750–850 °C. A slow temperature increase in a vacuum before nitriding is assumed to have the same effect as preheating [30].

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