PAPER

Analysis of the mechanical properties and microstructure of titanium surfaces designed by electromagnetic induction nitriding

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Abstract

Nitride has high hardness and excellent wear resistance. It is frequently prepared on a material surface to improve material performance. The nitriding layer can be prepared in different ways, so the bonding strength and microstructure between the nitriding layer and the matrix differ, which will directly affect the surface mechanical properties of the material. In this study, pure titanium (TA1) was nitrided using electromagnetic induction nitriding, and the microstructure of nitriding layer was analysed using x-ray photoelectron spectroscopy (XPS), scanning electron microscopy-electron backscatter diffraction (SEM-EBSD) and scanning electron microscopy-energy-dispersive x-ray spectroscopy (SEM-EDS). In addition, the mechanical properties of the nitriding layer were studied using a nanoindentation and scratch tester. The experimental result shows a 20 μm induction nitriding layer composed of TiN, Ti2N and α(N)-Ti. The compound layer (Ti2N and TiN) was approximately 3 μm. The surface was contaminated with C and O elements, and evident segregation bands were found between the induction nitriding layer and matrix. The induction nitriding layer can considerably improve the wear resistance of titanium alloy, but the bonding force between the induction nitriding layer and matrix decreases owing to the segregation band.

1. Introduction

Titanium (Ti) alloy is widely used in biomedicine owing to its low elastic modulus, excellent strength and good biocompatibility [1, 2]. However, its surface hardness and wear resistance are poor, leading to the premature failure of components. The nitride ceramic coating has excellent mechanical properties, corrosion resistance and high chemical stability [3]. It also has a positive impact on the biocompatibility of the implant surface [4] and tribological properties [5], thereby promoting cell proliferation near implants [6] and reducing tribocorrosion [7, 8] as well as allergic reactions [9]. Thus, the nitriding layer has been successfully applied in the biomedical field [5, 10].

Currently, various methods for preparing nitriding layers are used. These include chemical vapour deposition [3], laser nitriding [11] and plasma nitriding [12]. In this study, the electromagnetic induction nitriding technology, which is simple and fast, was used for performing surface nitriding treatment on Ti alloy. Studies [7, 8] have shown that an effective nitriding layer on the Ti alloy surface can quickly be prepared using electromagnetic induction nitriding technology. This technology has high efficiency, compatible with parts of all shape, causes zero pollution, and uses blind hole treatment. The induction nitriding layer is similar to the nitriding layer prepared using plasma nitriding, laser nitriding and other technologies. However, the differences lie in the thickness and microstructure between the nitriding layers prepared using different methods [13, 14], which will affect the mechanical properties of the nitriding layer.

Unlike that of the multi-phase nitriding layer, the hardness of the single-phase TiN layer greatly differs from that of the matrix, which is prone to brittle fracture [15, 16]. Therefore, the multi-phase nitriding layer with a hardness gradient has become a research hotspot. A study [8], through x-ray diffraction (XRD), proved that the
The induction nitriding layer is a gradient nitride structure composed of various nitrogen–titanium compounds with excellent mechanical properties. The nanoindentation technique can measure in situ the mechanical properties of engineering materials on the nanometre scale without disrupting their microstructure [17]. The scratch test can be used to measure the materials under the combined actions of the normal and tangential composite stresses [18]. The combination of the nanoindentation and scratch tests will help further understand the mechanism of the material structure influence on properties [19].

Studies [7, 8] have proved that induction nitriding can effectively improve the corrosion and wear resistances of titanium alloys, but the research on its microstructure is missing insufficient. Therefore, this study continues the research [8]. The chemical state and the microstructure of the induction nitriding layer are further observed and analysed using XPS, SEM–EDS and SEM–EBSD. The mechanical properties of the induction nitriding layer are tested using the nanoindentation technology and scratch test. The damage mechanism of the nitriding layer is discussed.

2. Materials and methods

2.1. Sample preparation
The medical pure titanium alloy (TA1) was acquired from Baoji Longqiangfeng Titanium Industry Co, its size was $\phi 16 \text{ mm} \times 8 \text{ mm}$. The chemical composition (in wt%) has a mass fraction of $\text{Fe} < 0.10$, $\text{C} < 0.3$, $\text{N} < 0.012$, $\text{H} < 0.008$, $\text{O} < 0.10$, and the remainder is Ti. The sample was polished using SiC sandpaper from 600 # to 3000 # and further polished using $2.5 \mu \text{m Al}_2\text{O}_3$ polishing, then washed with a JP-030S ultrasonic cleaning instrument (Shenzhen Jiemeng Cleaning Equipment Co. LTD) for 10 min. The prepared sample was treated with self-made high-frequency electromagnetic induction heating device, which was the same as before [8]. The following nitriding process parameters: the high-purity nitrogen pressure was $-30 \text{ kPa}$, the treatment temperature was $850^\circ \text{C}$ and the treatment time was 1 h.

2.2. Microstructure analysis
The chemical composition of the nitriding sample was analysed by XPS (PHI 5000 Versaprobe III, ULVAC Physical Electronics). During the XPS investigations, the pressure was maintained at $8 \times 10^{-10} \text{ Pa}$ in the analysis chamber. A monochromatic Al Kα x-ray source (1486.6 eV) was used. The electron take-off angle was $45^\circ$, and the pass energy was $69 \text{ eV}$. The step size was $0.125 \text{ eV}$. All spectra peaks were calibrated by the C 1s peak at 284.6 eV of binding energy. The cross-section morphology and phase structure of the nitriding sample were observed using a scanning electron microscope with an electron backscattered diffraction system (Aztec Nordlys Max3, Carl Zeiss AG, Germany). Accordingly, EBSD maps were acquired with 5 kV accelerating voltage, $3 \mu \text{m}$ scan step size and $15 \text{ mm}$ working distance. The sample was prepared using an argon ion polisher. Subsequently, the element distribution of the sample cross-section was analysed using SEM–EDS (SU8010, Hitachi., Ltd).
2.3. Mechanical property testing

The nanoindentation hardness (H) and elastic modulus (E) of the sample cross-section were measured using a nanoindentation instrument (UNHT, Switzerland CSM Instruments Co., Ltd) with a diamond Berkovich indenter. A maximum load of 1.0 mN was applied for 5 s. Ten indentations were tested at a regular intervals of 3.0 μm. The Scratch test was performed to measure the adhesion strength and the brittleness of the sample surface and the cross-section in different ways, i.e. progressive and constant load scratch tests. The sample surface was tested using the progressive load scratch test. The end load (Fn), loading rate, speed and length were set as 30 N, 60 N min⁻¹, 4 mm min⁻¹ and 2 mm, respectively. Ft is the force of friction which the scratch produces. The cross-section of the nitriding sample was tested using the constant load scratch test. The constant loads were 1, 3 and 5 N. The speed and length were 0.3 mm min⁻¹ and 0.15 mm, respectively.

3. Results and analysis

3.1. XPS

In the study [8], the XRD results confirmed a large number of nitrogen–titanium compounds on the surface of the induction nitriding layer. Here, XPS was also used to study the surface structure of the induction nitriding layer and further understand the elemental composition and chemical state of the induction nitriding layer. Figure 1 presents the XPS spectrum of the nitriding layer. Accordingly, Ti, N, C and O elements can be found. The strongest peak of Ti was Ti 2p, and those of N, O and C, and all of were 1s. CaseXPS software is used to fit them by peaks (figure 2) to better understand the energy state of each element.

Figure 2(a) shows the narrow scan spectra of the Ti element. A strong peak identified as the Ti 2p₃/₂ peak can be found at the position where the binding energy was 454.7 eV. The electrons in an atom have orbital and spin motions, and the coupling between them makes the energy level split [20]. The spin–orbit splitting for the Ti 2p peak produced the Ti 2p₃/₂ and Ti 2p₁/₂ peaks. The energy difference between them was 5.78 ± 0.04 eV; hence the Ti 2p₁/₂ peak position was at 460.6 eV binding energy. Accordingly to [21], the peaks at the binding energies of 454.7 and 460.6 eV corresponded to the Ti–N bond in TiN. Similarly, the peaks at the binding energies of 457.8 and 463.2 eV corresponded to the Ti–O bond in TiO₂. In addition, an accompanying peak that was approximately 2 eV away from the main photoelectron peak (454.7 eV) was also found. Bertoia [22] claimed that this result was caused by the reaction of TiN with O to form TiNxOy compounds. The ionic radius of O and N
are similar; thus, they exist as solid solutions in the TiO–TiN system. This accompanying peak represented the TiNx–Oy bond. Figure 3(b) shows the narrow scan spectra of the N element composed of two peaks with binding energies of 396.9 and 399.5 eV. The strongest peak (396.9 eV) represents the N–Ti bond, whilst the peak at 396.9 eV can be caused due to the N–O bond in TiNxOy. Figures 3(c) and (d) show the narrow scan spectra of the O and C elements, which are surface-contaminating elements in the material; hence, they are also on the surface of the induction nitriding layer.

3.2. SEM–EBSD
The first surface layer of the nitriding layer has a TiN structure, as shown by the XPS result. The SEM–EBSD technology was used to further study the phase recognition and structure of the nitriding layer cross-section and comprehensively analyse the nitriding layer structure (figure 3). The compound layer was approximately 3 μm
and it is mainly composed of titanium nitrides Ti$_2$N and TiN. Nitrogen is a stable element of $\alpha$-Ti and has a high solubility in the $\alpha$-Ti phase, hence it forms a solid solution ($\alpha$(N)-Ti) in the $\alpha$-Ti phase as an interstitial atom. Therefore, the $\alpha$(N)-Ti phase was not found in the SEM-EBSD. An peak of the $\alpha$(N)-Ti phase was observed in XRD\cite{8}. The nitriding layer formation on the Ti alloy surface is a complex process that involves multiple reactions at the boundary between gas and metal and inside the matrix. The dynamics of nitride diffusion in Ti alloys has been studied and a growth model of the nitriding layer has been proposed\cite{23}. When Ti alloy is in a high-temperature environment with active N atoms, which will first be solid dissolved in Ti alloy surface as interstitial atoms the $\alpha$(N)-Ti layer is formed. When the nitrogen concentration at the metal interface is higher than $\alpha$(N)-Ti layer, the Ti$_2$N layer will be formed at the interface. Similarly, the nitrogen concentration at the metal interface is higher than that in the Ti$_2$N layer, and the TiN layer is formed\cite{24}. The model is also applicable to the induction nitriding of Ti alloy. TiN, Ti$_2$N and $\alpha$(N)-Ti are formed on the Ti alloy surface from the surface to the inside, indicating that the induction nitriding layer has a gentle gradient of the nitrogen concentration. Table 1 shows that the TiN phase accounts for 21.51% of the total and is the main phase of the compound layer. This further confirms the previous research results\cite{8}.

Figures 3(c) and (d) depict the crystal orientation diagrams of the nitriding layer showing the twins generated in the TiN layer. Twins were generated because the eddy current effect generates much heat on the Ti alloy surface during the induction nitriding. This is coupled with the induction magnetic field and the nitrogen atoms diffusion, resulting in a substantial increase in the inner surface energy. Consequently, the microstructure relative motion of the atoms in $\alpha$-Ti lattice occurs. Twins are formed during the cooling after the induction nitriding to adapt to the internal variation and stress state of the material. The crystal structure of the hexagonal system ($\alpha$-Ti) is determined using the following lattice parameters: $a = 2.95$ Å; $c = 4.73$ Å; cubic crystal system (TiN): $a = 4.24$ Å and tetragonal system (Ti$_2$N): $a = 4.94$ Å; $c = 3.04$ Å.

### 3.3. Nanoindentation

According to study\cite{8}, the nitriding layer thickness was approximately 20 $\mu$m. The SEM-EBSD results showed that the compound layer was only approximately 3 $\mu$m in the nitriding layer, indicating that the $\alpha$(N)-Ti layer was dominant with a thickness of approximately 17 $\mu$m. The sample was tested by a nanoindentation instrument to explore the influence of the microstructure on the mechanical properties of the nitriding layer. First, the data of the 10 points were collected on the nitriding layer cross-section (figure 4). The compound layer was only 3 $\mu$m; thus, the first indentation point was 2 $\mu$m. Base on this, each point added 3 $\mu$m. The second indentation

| Phase          | Total faction(%) |
|----------------|------------------|
| $\alpha$-Ti    | 53.08            |
| $\beta$-Ti     | 0.50             |
| TiN            | 21.51            |
| Ti$_2$N        | 6.29             |

Figure 5. The Cross-section SEM and mapping of the nitriding sample.

Table 1. Phase composition of induction nitriding layer.
The figure also illustrates that the indentation depth increases with the increase of the indentation point distance. However, the eighth point was singular (curve 8) and approximately located in the 23 μm nitriding layer section. A mapping analysis was performed to determine the cause of singularity (figure 5). The results showed a segregation zone between the nitriding layer and the matrix. The nitriding layer formation led to the enrichment of Fe and O in the transition layer and formed a banded distribution between the nitriding layer and the matrix. In induction nitriding, the affinity of Ti and N is strong, so the nitriding layer and the nitrogen interstitial solid solution layer are rapidly formed under the eddy current effect of induction heating. The diffusion activation energy of Fe is low, N occupies the original position of Fe, and it is pushed to the junction of the induction nitriding layer and matrix to form a segregation band.

Table 2. Mechanical properties of cross-section nitriding sample.

| Points | Elastic modulus, E/GPa | Nanohardness, H/GPa | H/E | (H²/E²)/GPa |
|--------|------------------------|---------------------|-----|-------------|
| 1      | 174.05                 | 18.74               | 0.1077 | 0.2173    |
| 2      | 151.06                 | 15.61               | 0.1033 | 0.1667    |
| 3      | 140.53                 | 13.48               | 0.0959 | 0.1240    |
| 4      | 138.86                 | 11.85               | 0.0853 | 0.0863    |
| 5      | 143.90                 | 13.74               | 0.0955 | 0.1253    |
| 6      | 129.04                 | 9.93                | 0.0769 | 0.0588    |
| 7      | 121.58                 | 6.82                | 0.0561 | 0.0215    |
| 8      | 68.41                  | 2.06                | 0.0380 | 0.0019    |
| 9      | 90.16                  | 4.03                | 0.0447 | 0.0081    |
| 10     | 95.23                  | 4.18                | 0.0439 | 0.0081    |

Figure 6. Optical micrograph of the sample scratch track (a) untreated sample (b) nitriding sample.

Figure 7. (a) Scratch depth curves (b) Force of friction curves.
Therefore, the indenter bounce phenomenon occurred at 500 μm. Material stacking caused by the plastic deformation hindered the movement of the indenter after accumulating, hence, plastic deformation occurred when the load force reached a certain value. The strain hardening and the elastic modulus are important parameters for evaluating the mechanical properties of materials. Table 2 shows that the $H / E$ and $H^3 / E^2$ of the nitriding layer decrease with the indentation point depth, indicating that the induction nitriding layer is a gradient strengthening layer.

3.4. Micro scratches

Figure 6 depicts the surface scratch of the untreated and nitriding samples. Figure 7 illustrates the obtained data. The depth of the scratches increased with the increasing applied load. The untreated surface was relatively soft; hence, plastic deformation occurred when the load force reached a certain value. The strain hardening and the material stacking caused by the plastic deformation hindered the movement of the indenter after accumulating to a certain extent. Therefore, the indenter bounce phenomenon occurred at 500 μm. Figure 6(a) displays that there are cracks perpendicular to the sliding direction in the scratch area, which were generated by the tensile stress of the indenter under dynamic contact [26]. Owing to the increases in the applied load, the internal stress of the scratch groove and crack density increased, and wider cracks appeared. Figure 6(b) shows the scratch on the nitriding sample surface. This scratch is shallow, gentle and smooth without fragmentation and stratification, indicating that the nitriding layer with a gradient structure has excellent adhesion to the matrix [18]. The lines in the grooves of the nitriding sample propagated along the scratch direction. Moreover, the energy was mainly dissipated through the generation of the dislocation in the TiN grains and the shearing between the TiN grains [27].

Figure 7(a) shows the curve of the scratch depth–length. The scratch depth of the nitriding sample slowly increased with the applied load force increase its maximum depth was 12 μm without the bounce phenomenon. In contrast, the scratch depth of the untreated sample non-linearly increased with the applied load force increase. The scratch process has different energy dissipation mechanisms. The material stacking and strain hardening caused by the plastic deformation will produce abnormal contact points between the indenter and the material, which will result in changes in the local depth and friction. The maximum scratch depth of the untreated sample was 26 μm, which is 2.17 times that of the nitriding sample. Figure 7(b) depicts a scratch friction–length curve showing a trend that is similar to that in figure 7(a). The maximum friction force of the nitriding sample was 6.12 N, whereas that of the untreated sample was 23.79 N, which is 3.89 times that of the nitriding sample. Therefore, compared with the untreated sample, the nitriding layer has better wear resistance. Further, the structure between the nitriding layer and matrix showed gradient evolution, which can effectively resist strain damage and reduce the possibility of the nitriding layer rupture.

1, 3 and 5 N constant load scratch test was performed on the cross-section of the nitriding sample with a micro-scratch tester to further study the mechanical properties of the induction nitriding layer. The scratch length was 150 μm. Different tensile and shear stresses are generated on the section when the cross-section of the nitriding sample is subjected to normal and tangential stresses. Shear stress promotes plastic deformation and is the driving force of the dislocation movement. The tensile stress promotes crack propagation. Therefore, the matrix will begin to undergo plastic deformation after the scratch starts, and the scratch width will widen with the load increase. When the induction nitriding layer was scratched, the deformation mechanism changed owing to the change in the microstructure. At this point, an acoustic emission (AE) mutates. First, a weak AE was generated at approximately 10 μm from the surface under low load (figure 8(a)). At that time, a tiny crack was generated in the nitriding layer. Next, a strong AE was generated at approximately 5 μm from the surface,

![Figure 8. The cross-section nitriding scratch track optical micrograph and acoustic emission (a) 1 N (b) 3 N (c) 5 N.](image)
indicating that the nitriding layer fractured along 60° to the scratch direction. The first AE was generated at a distance of 20 μm from the surface (segregation zone) when the load force was increased to 3 N. Owing to the segregation zone, the bonding force between the nitriding layer and the matrix decreased, and the nitriding layer failed and fell. With continuous sliding, the indenter reached the edge of the sample, and the AE suddenly changed. Under the 5 N load force, the stress and strain increase caused material stacking, which led to the fall of the nitriding layer earlier (50 μm from the surface). The peeling notch also became closer to the inside. Under a different constant load, the fracture angles of the nitride layer were about 60°, indicating the same fracture mechanism. With the load increase, the nitriding layer peeling moved forward, and the segregation zone generation led to a decrease in the bonding force of the nitriding layer.

Figure 9(a) shows the scratch depth–length curve of the nitriding sample cross-section. The scratch depth increased with the load increase. The 1 N curve illustrates the indenter begins to contact the nitriding layer, which is approximately 20 μm away from the section (nitriding layer thickness). This resulted in the depth curve reduction. Crack generation or nitriding layer peeling will lead to abrupt changes in the curve. From the scratch friction curve of the nitriding sample section (figure 9(b)), the friction force also increased with the load increase. The friction force of the curve increase when cracks occur or when the nitriding layer falls off. The phenomenon shown in figure 8 corresponds to this.

4. Conclusion

The following conclusions were drawn from this study:

1. The induction nitriding layer was a 20 μm thick layer and composed of TiN, Ti2N and α(N)-Ti from the outside to the inside. The compound layer was approximately 3 μm. Twins were produced in this layer. The outermost layer (TiN layer) of the nitriding layer which was the TiN layer of nitriding layer was polluted by C and O elements, with the pollution degree be at the nanometer level.

2. The H/E and the H^2/E^2 of the induction nitriding layer decreased with the depth of the indentation point. The induction nitriding layer is a gradient strengthening layer with a multi-phase structure. A segregation zone was generated between the nitriding layer and the matrix, which had little influence on the surface nitriding layer. The bonding force of the nitriding layer decreased owing to the generation of segregation layer.

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