Mechanical Properties of Type 304 Austenitic Stainless Steel Coated with Titanium Nitride after Ion-Nitriding[†]

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Austenitic type 304 stainless steel was ion-nitrided at 823–853K, using a N_2-H_2 d.c. glow discharge plasma. After ion-nitriding, the top thin compound layer mainly composed of $\gamma'-Fe_4N$ was removed by emery paper. A thin layer of Ti with a thickness of $0.1\ \mu m$ was deposited on this nitrided specimen and, subsequently, TiN of $1.7\ \mu m$ was deposited at about 623 K, using an ion-plating technique. By this combined treatment of ion-nitriding and subsequent ion-plating, surface hardened layers were formed, which were composed of (i) a thin outermost coating layer of TiN with the hardness of about $Hv\ 2200$ and (ii) a thick inner diffusion layer of about $Hv\ 1100$.

The mechanical properties of the specimens TiN-coated after ion-nitriding were examined and compared with the untreated or only ion-nitrided or only TiN-coated specimens. The duplex treated specimens showed an improved resistance to wear, the largest wear resistance among them. As for the corrosion resistance, the specimens were a little inferior to the only TiN-coated specimens, but showed an improved resistance compared with the untreated specimens. The fatigue limit of the specimens was lowered slightly compared with the only ion-nitrided specimens, but showed a considerable improvement compared with the untreated specimens.

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I. Introduction

The ion-nitriding⁽¹⁾⁻⁽¹¹⁾, utilizing a N_2-H_2 glow discharge plasma, is one of the effective methods for the surface hardening of steels. By this treatment, the diffusion layer with a high hardness is formed on the specimen surface and the resistivity to wear and fatigue is improved. This treatment has many advantages such as no environmental pollution and saving energy unlike conventional salt bath nitriding⁽¹²⁾⁻⁽¹⁵⁾ or gas nitriding. So, it is becoming the main current of nitriding method for the surface treatment of machine parts, tools and metal molds. However, the improvement of the corrosion resistance is not necessarily enough. Especially, in the case of stainless steels, it has been indicated that the corrosion resistance becomes worse inversely⁽⁴⁾⁽⁵⁾⁽⁸⁾.

Recently, PVD (physical vapor deposition) method has been developed at a low temperature between about 573 K and 773 K. Especially, TiN ceramic coating⁽¹⁶⁾⁻⁽³⁵⁾ is applied to cutting tools, metal molds, and also frames of spectacles and watches for decoration. As for the characteristic of TiN ceramic coating, it shows very high hardness and is superior in corrosion resistance, antiseizure properties, ornamental purposes and so on. However, since the coating layer is thin, a few microns, and brittle, the adherence to the substrate and shock-resistance have

been a subject of investigation. For example, in the case of coating onto hardened steels by heat treatment like cutting tools, the coating is effective. On the other hand, in the case of coating onto unhardened ordinary metals, as the cracking occurs in TiN films owing to the plastic deformation of substrates, the good effect of TiN film cannot be achieved. Therefore, the surface hardening will be effective as the pre-treatment of TiN-coating. In the present case, an use of ion-nitriding is convenient for surface hardening treatment, because the ion-nitriding is the same plasma techniques as TiN-coating method. The effect of nitriding as the pre-treatment of TiN-coating is scarcely reported. For example, there are papers⁽¹⁸⁾⁽¹⁹⁾ that plasma nitriding was done at a relatively low vacuum, followed by TiN-coating by an ion-plating technique in the same equipment. Other investigations reported that an thick TiN film was deposited by CVD method at a high temperature of 1273 K after ion-nitriding⁽²⁷⁾ and that the adherence to the substrate was improved by ion-implantation of N^+ ⁽³⁰⁾. But the mechanical properties of these films are not examined sufficiently.

The object of this work is to elucidate the effect of duplex surface treatment. Austenitic type 304 stainless steels are duplex surface treated by the ion-nitriding and subsequent ion-plating of TiN. The variations of the resistance to wear, corrosion and fatigue are examined.

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II. Experimental Procedures

1. Preparation of specimens

A rod of commercial type 304 stainless steel was used. The chemical compositions are given in Table 1.

The specimens for the wear test and the corrosion test are prepared as follows. The rod was cut into the disc 20 mm in diameter and 8 mm thick. And these were polished with emery paper until #1200 and diamond paste (averaged grain size of $3\mu\text{m}$). The specimens thus prepared were called the untreated ones hereafter. After the cleaning in acetone, these specimens were ion-nitrided by a $\text{N}_2\text{-H}_2$ d.c. glow discharge in an equipment described in Ref. (6). The nitriding conditions were as follows: discharge gas; 80 vol% N_2 + 20 vol% H_2 , pressure; 665 Pa, nitriding temperature; 853 K, nitriding time; 7.5 ks. The surface compound layers formed during the ion-nitriding were removed by emery paper until #1200 and then polished with diamond paste ($3\mu\text{m}$). These specimens were called the nitrided ones hereafter.

TiN film was formed by the arc discharge type high vacuum ion-plating equipment (Shinko Seiki Co., Ltd.). The vacuum bell jar of this equipment is 1100 mm in diameter and 800 mm in depth. The specimens were rotated and revolved around the horizontal axis in this bell jar. The untreated or nitrided specimens were cleaned in flon and then evacuated to about 1×10^{-4} Pa by a diffusion pump in this bell jar. These specimens were rotated at an angular velocity of 1.8 rad/s and revolved at an angular velocity of 0.1 rad/s, keeping about 390 mm from the surface of the evaporation source in the crucible. The specimens were cleaned by ion-bombardment using a H_2 discharge plasma at a pressure of 27 Pa for 1.2 ks and subsequent Ar discharge plasma at a pressure of 5 Pa for 0.6 ks at the respective discharge voltage of 1 kV. Commercial titanium of above 97% purity was then melted with an electron gun deflected by 1.5π rad at a power of 6 kW (10 kV, 600 mA) and vacuum-deposited onto the surface to the thickness of about $0.1\mu\text{m}$. This pure Ti layer aims at improving the adherence of $\text{TiN}^{(31)}$. Next, N_2 was introduced at a pressure of 2×10^{-2} Pa and TiN was deposited at an ionizing voltage of 35 V and a substrate voltage of -400 V. The specimens were heated up to about 623 K by a carbon heater located in a vacuum bell jar and an ion-bombardment. TiN-coated specimens onto the surface of the untreated ones were called TiN-coated ones, and those onto the nitrided ones were called duplex treated ones.

The methods of preparation of specimens for the fatigue test are as follows. The specimen for the fatigue

Fig. 1 Shape and dimensions (in millimeters) of the specimen for the fatigue test.

test was smoothly polished and the diameter of its uniform section was 10 mm as shown in Fig. 1. Its surface was polished with #3000 emery paper and then electropolished in an electrolytic solution of 10 vol% perchloric acid and 90 vol% acetic acid. The specimens prepared until this surface condition were called the untreated ones. The specimens cleaned in acetone were ion-nitrided in an ion-nitriding apparatus where the large size specimens could be installed (an effective diameter of 500 mm and a height of 1000 mm, Research Institute for Applied Sciences). The nitriding conditions were as follows: discharge gas; 40 vol% N_2 + 60 vol% H_2 , pressure; about 730 Pa, nitriding temperature; 823 K, nitriding time; 43.2 ks. The ion-nitrided specimens were polished by #3000 emery paper and then by a diamond paste ($1\mu\text{m}$) in order to remove the surface compound layer. The specimens in this surface condition were called the nitrided ones. And then, TiN was deposited using an ion-plating technique onto the surface of the untreated or nitrided specimens. The coating conditions were the same as those for the wear test. That is, the intermediate layer of Ti was deposited by about $0.1\mu\text{m}$ and at a temperature of about 623 K. The TiN-coated untreated specimens were called the only TiN-coated ones, and the TiN-coated nitrided specimens were called the duplex treated ones. Further, the untreated specimens were vacuum-annealed at 623 K for 7.2 ks before the fatigue test in order to give the same thermal career.

2. Methods for the evaluation

The physical properties of these surface-treated specimens such as surface topography, micro-structure, crystal structure, and hardness were examined using an optical microscope, SEM, an X-ray diffractometer and a micro-vickers hardness tester. For metallographic examination of the specimens, an etching solution of 6 mass% ferric chloride-3 mass% hydrochloric acid-91 mass% ethanol was utilized.

For these specimens, the resistance to wear, corrosion and fatigue were examined. The wear resistance was evaluated with an Ohgoshi type wear testing machine. In this machine, a rotating wheel was pressed against the flat specimen at a constant contact pressure and wear loss was obtained from the width of an wear track on the specimen surface. In the literature⁽¹⁷⁾⁽²⁵⁾⁽²⁶⁾, applications of this machine for the TiN film are reported. The wheel was made of austenitic type 304 stainless steel and the friction velocity was constant at 0.51 m/s with a final load of

Table 1 Chemical composition of type 304 stainless steel used in this work (mass%).

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Co
0.056	0.53	1.81	0.037	0.025	8.26	18.36	0.18	0.43	0.17

21 N. The wear test was performed without a lubricating oil at a room temperature in air. The wear resistance was evaluated from the wear losses which were obtained during the sliding distance of 600 m. The corrosion resistance was estimated from the current density which was obtained from the polarization curve tested in 0.5 kmol/m³ H₂SO₄ aq. solution at about 293 K using a potentiostat. Similar measurements for the TiN film have been reported by other workers^{(22)–(24)(32)(33)}. A mercury sulfate electrode (Hg|Hg₂SO₄|H₂SO₄(0.5 kmol/m³)) was utilized for the reference electrode and a platinum plate for the counter electrode. The working electrode was covered with an epoxy resin except for the measuring area of 6 millimeters square. The natural potential of the specimen was measured in bubbling N₂ gas through the solution. Its working electrode was polarized to the cathodic and then anodic direction, and the current density was measured after its current was fully stabilized. The fatigue test was carried out in air with an oil-pressured servo type fatigue testing machine (max. load 100 kN) under the axial load of the tension-compression condition. The S–N curves which indicate the relation between the stress amplitude and the number of cycles to failure were obtained. The cyclic load was of a sinusoidal form with a frequency of 2–4 Hz. The rotating-bending fatigue test are already reported for TiN film⁽³⁴⁾⁽³⁵⁾.

III. Experimental Results and Discussion

1. Physical properties of the nitrided layer and TiN film

The thickness, microstructure and hardness of the nitrided layer and TiN film were investigated for these surface-treated specimens. Figure 2 shows the structure of the cross section of the duplex treated specimen. The white layer at the left in Fig. 2 corresponds to the TiN film. The dark etched region adjacent to the TiN film is a nitrided layer and the innermost region is an unhardened matrix. The hardness which was measured from the surface of the nitrided layer is about *Hv* 1100. On the other hand, the hardness in the diffusion layer shows between *Hv* 900 and 1000, and beyond the nitriding front it decreases rapidly to the hardness of the untreated specimen of *Hv* 200. The hardness profile of the nitrided layer was almost unchanged before and after TiN-coating. From the observation of the cross sections, the thickness of the nitrided layers was 55 μ m for the disc type specimens of the wear and corrosion tests, and for the specimen of the fatigue test, its thickness at the section with a diameter of 10 mm showed uniform and 120 μ m. Since the averaged grain size of the matrix is about 60 μ m, the former thickness is almost the same as the grain size of the matrix and the latter is almost twice. Total thickness of the coating layer is 1.8 μ m and the thickness of an intermediate layer of Ti is almost 0.1 μ m, so that of TiN film equals to 1.7 μ m. The thickness and the uniformity of the coating layer was checked from the specimen surface with a fluorescent X-ray film thickness

Fig. 2 Microstructure of the specimen ion-nitrided at 853 K for 7.5 ks and then coated with TiN.

Fig. 3 X-ray diffraction patterns taken from the specimens (a) only coated with TiN and (b) ion-nitrided at 853 K for 7.5 ks and then coated with TiN.

measuring equipment and the same values were obtained. The uniformity of the thickness of TiN film for the specimen of the fatigue test was particularly confirmed.

X-ray diffraction patterns were taken from the specimen surfaces using an X-ray diffractometer (CoK α radiation, 20 kV-12 mA). Figure 3 shows X-ray diffraction patterns taken from the specimens TiN-coated in the same condition onto (a) the untreated substrate and (b) the nitrided one. As shown in Fig. 3(a), diffraction lines of γ phase of the substrate are observed and it is noted that TiN is preferentially oriented in the direction of (111) plane. Figure 3(b) indicates that the half width of the diffraction peak of γ phase of the substrate is broadened because of the solid solution of nitrogen and, further, α phase is formed. In this figure, γ :N and α :N mean that these phases contain the nitrogen. The diffraction peaks of iron nitrides of γ' -Fe₄N and ϵ -Fe₂₋₃N are not observed, since the surface compound layer is removed as mentioned earlier. The diffraction peaks of TiN are same in (a) and (b), so it is proved that crystal structures are same in these TiN layers.

Fig. 4 Load dependence of the vickers microhardness for the specimens (a) untreated, (b) ion-nitrided, (c) only TiN-coated and (d) duplex treated.

Figure 4 shows the dependence of the vickers microhardness which was measured from the specimen surface on the indentation load of micro-vickers hardness tester. In this figure, (a), (b), (c) and (d) correspond to the untreated, nitrided, only TiN-coated and duplex treated specimens, respectively. From this figure, it is found that the surface hardness of the specimens untreated and nitrided is about Hv 200 and Hv 1100, respectively, and the hardness of TiN film is estimated to be about Hv 2200 from the hardness at the light indentation load. The cracks occurred at the walls and the circumferences of indentation traces because of the high hardness and the brittleness of the TiN film. The cracks occurred at about 0.1 N in the case of the untreated substrate and at about 1 N in the case of the nitrided one, so it is clear that the crack-initiating load in the untreated substrate is smaller than that in the nitrided one and the number of cracks in the former is large compared with that in the latter. Figure 5 shows optical micrographs of the indentation traces. Figure 5(a) is the indentation trace at a load of 0.25 N for the only TiN-coated specimen, and many cracks are observed at the circumferences and on the walls parallel to the edges of the indentation trace. Figure 5(b) corresponds to the nitrided substrate and cracks are hardly observed in spite of a larger indentation load of 1 N. The reason why many cracks occurred in the untreated substrate is due to the ease of the plastic deformation of the substrate and a small adhesion of TiN film to this substrate. Figure 5(c) shows the plastic deformation which was formed at the indentation load of 1 N for the untreated specimen. In this figure, the circumferences of the indentation trace protrude fairly and slip lines occurred. It can be seen that the circular crack occurred at the circumferences of the indentation trace is due to the tension in this film caused by this protrusion. The adhesion of TiN film to the nitrided substrate appears to be better compared with that to the untreated substrate, since the number of cracks on the walls of the indentation traces which are of the same size is few in the case of the nitrided substrate.

Fig. 5 Optical micrographs of the typical shapes of indentations for the specimens (a) only TiN-coated (0.25 N load), (b) duplex treated (1 N load) and (c) untreated (1 N load).

2. Mechanical properties of the specimens after the surface treatment

(1) Wear resistance

Using an Ohgoshi type wear testing machine, the relation between the sliding distance and the wear loss is examined for the surface-treated specimens. Figure 6 shows wear losses against the sliding distance up to 600 m for the specimens (a) untreated, (b) nitrided, (c) only TiN-coated and (d) duplex treated. From this figure, it can be seen that the wear loss decreased remarkably and thus the wear resistance is improved by ion-nitriding. The wear loss decreases still more in the case of TiN-coating after ion-nitriding, the duplex treated specimen. However, in the case of only TiN-coating, its wear loss becomes larger than that of the untreated specimen at an increasing sliding distance. As in the case of cracks in the circumferences of indentation traces, the untreated substrate is easily plastically deformed and cracks are formed in TiN film at the border where the wheel rushes into the specimen. So, the wear dust of TiN is formed and the wear loss of the only TiN-coated specimen increases because of its abrasive action.

Curves going through the origin in this figure were obtained using a least square method of the measured values. Specific wear volumes were compared using the

Fig. 6 Wear loss as a function of sliding distance for the specimens (a) untreated, (b) ion-nitrided, (c) only TiN-coated and (d) duplex treated. Sliding speed; 0.51 m/s. Final load; 21 N.

wear losses at a sliding distance of 600 m. These values are $1.6 \times 10^{-13} \text{ m}^2/\text{N}$, $1.9 \times 10^{-13} \text{ m}^2/\text{N}$, $4.9 \times 10^{-14} \text{ m}^2/\text{N}$ and $3.2 \times 10^{-14} \text{ m}^2/\text{N}$ for the untreated, nitrided, only TiN-coated and duplex treated specimens, respectively. From these values, it can be seen that the specific wear volume for duplex treated specimens decreases to 1/5.

(2) Corrosion resistance

It is known that ion-nitrided stainless steels show the inferior corrosion resistance, since CrN is precipitated in the nitrided layer and the content of free Cr decreases. However, authors⁽⁶⁾ have reported that austenitic type 304 stainless steel is ion-nitrided at a low temperature of about 623 K without the precipitation of CrN using 20 vol% N_2 + 80 vol% H_2 discharge gas and it has the surface hardened layer composed of f.c.t. nitride of Y_N with a hardness of H_v 1500. This specimen shows the fairly small deterioration of corrosion resistance. Figure 7 shows polarization curves tested in 0.5 kmol/ m^3 H_2SO_4 aq. solution using a potentiostat in order to examine the variation of the corrosion resistance due to surface treatments. The abscissa of Fig. 7 is altered to the potential of hydrogen electrode. These curves are for the specimens (a) untreated, (b) nitrided at 853 K, (e) low temperature-nitrided at about 623 K and (f) low temperature-nitrided and then vacuum-annealed at 823 K for 7.2 ks. By comparing the anodic polarization curve of Fig. 7(a) with that of (b), it is seen that the nitrided specimen shows an increase in the current density by more than two orders and thus the deterioration of the corrosion resistance. On the other hand, by comparing anodic polarization curve of (a) with that of (e), it is concluded that low temperature-nitrided specimens show the increase in the current density by about one order and the deterioration of the corrosion resistance is fairly small. Although the nitrided layer with a fairly good corrosion

Fig. 7 Potentiostatically determined polarization curves tested in 0.5 kmol/ m^3 H_2SO_4 aq. solution for the specimens (a) untreated, (b) ion-nitrided at 853 K, (e) ion-nitrided at about 623 K and (f) ion-nitrided at about 623 K and then vacuum-annealed at 823 K for 7.2 ks.

Fig. 8 Potentiostatically determined polarization curves tested in 0.5 kmol/ m^3 H_2SO_4 aq. solution for the specimens (a) untreated, (b) ion-nitrided at 853 K, (c) only TiN-coated and (d) duplex treated.

resistance and a high hardness is formed by low temperature-nitriding, this treatment has some problems that a long nitriding time is needed and the corrosion resistance deteriorates above 723 K owing to the disappearance of Y_N phase and the formation of α phase and CrN ⁽⁶⁾. For example, Fig. 7(f) is a result for the specimen nitrided at

a low temperature and then vacuum-annealed of 823 K for 7.2 ks. The current density of (f) increases compared with that of (e) and becomes to be nearly equal to that of (b).

Figure 8 shows the polarization curves tested in 0.5 kmol/m³ H₂SO₄ aq. solution in order to examine the effect of TiN film. In this figure, (a), (b), (c) and (d) correspond to the results for the specimens untreated, nitrided at 853 K, only TiN-coated and duplex treated. By comparing Fig. 8(a) with (c), it is seen that the only TiN-coated specimen shows a decrease in the current density by more than one order of magnitude, the improvement of the corrosion resistance. The current density for the duplex treated specimen (d) is slightly higher compared with that for the only TiN-coated specimen (c), but decreases by about one order of magnitude compared with that for the untreated specimen (a). The corrosion resistance of TiN-coated specimens will be controlled by the quality of the TiN film⁽²²⁾⁻⁽²⁴⁾. Recently, it is reported that an undercoating of Ti has a good effect on the improvement of the corrosion resistance⁽³²⁾⁽³³⁾. In the present experiment, coating was made with TiN-deposition of 1.7 μ m onto an intermediate Ti layer of 0.1 μ m. The resultant film will be compact and have a good adhesion to the substrate.

(3) Fatigue resistance

Figure 9 shows S-N diagrams obtained by the uniaxial fatigue test with a cyclic stress of tension-compression (sinusoidal form, 2~4 Hz). The abscissa indicates a number of cycles to failure, and the ordinate indicates a stress amplitude. In this figure, (a), (b), (c) and (d) correspond to the untreated, nitrided, only TiN-coated and duplex treated specimens, respectively. Fatigue tests were carried out using four specimens for each surface treatment.

The measured values (a) for the untreated specimens are within the same fluctuation range as reported in Ref. (36) and the fatigue limit is as about 230 MPa. In the case for the only TiN-coated specimen, the fatigue lives were extended slightly under stress amplitudes less than 270 MPa. As is reported in Ref. (34), the primary cause of this phenomenon is a restriction of plastic deformation at the specimen surface due to the adherent TiN film on the specimen surface and the occurrence of the fatigue crack is delayed. However, under a high stress of 290 MPa, many cracks occurred in the TiN film at the smaller number of cycles and its fatigue life was lowered compared with that of the untreated specimen. This suggests that the formation of cracks was initiated by the cracks of the TiN film.

As shown in Fig. 9(b), the fatigue limit is improved significantly by ion-nitriding. The fatigue properties of the nitrided specimens have been examined with the Tuftride-treated steels using a rotating-bending fatigue testing machine⁽¹²⁾⁻⁽¹⁵⁾. And it is pointed out that the specimen surface is strengthened and the compressive residual stresses are generated due to the formation of the surface hardened layer, which lead to an increase in

Fig. 9 S-N diagram showing uniaxial stress fatigue properties for the specimens (a) untreated, (b) ion-nitrided, (c) only TiN-coated and (d) duplex treated.

the fatigue limit. However, there are few reports as for the fatigue test under the axial load for the nitrided specimens⁽¹³⁾ or that for the nitrided stainless steel⁽¹⁴⁾. They reported that the fatigue limit is increased by ion-nitriding. The present test was carried out under the axial load and showed the marked improvement of the fatigue limit probably due to the same reason. Further, beyond the stress amplitude of 380 MPa, cracks were generated on the specimen surface at the early stage and the fatigue life was shortened. But, the fatigue life was increased rapidly below 370 MPa. The fatigue limit for the nitrided specimens is estimated at about 350 MPa from the results of the four test pieces shown in Fig. 9(b). On the other hand, the fatigue limit for the untreated specimen is estimated at about 230 MPa, so the fatigue limit is increased by about 1.5 by ion-nitriding. The duplex treated specimens of Fig. 9(d) showed a slight lowering of fatigue life compared with the nitrided specimens, but the S-N curve is similar with that of nitrided one. The reason why the fatigue life of the duplex treated specimen is lowered compared with that of the nitrided specimen can be interpreted as follows. That is, the internal strain is relieved due to the temperature rise until about 623 K during the deposition of TiN. Further, it is reported that the compressive residual stress is generated in the film in PVD-coating and the tensile residual stress corresponding to this compressive stress is generated in its substrate⁽²⁰⁾⁽²¹⁾, so the compressive residual stress induced in the nitrided layer by ion-nitriding is decreased. Although the fatigue life of the duplex treated specimen is slightly shortened compared with that of the nitrided specimen, its fatigue limit is estimated at about 330 MPa and increased by about 1.4 compared with that of the untreated specimen.

IV. Conclusion

Austenitic type 304 stainless steels were duplex surface-treated by ion-nitriding at 823~853 K and subsequent

ion-plating of TiN at about 623 K. TiN film is coated by about $1.7\ \mu\text{m}$ after the deposition of an intermediate Ti layer of about $0.1\ \mu\text{m}$. The following results are obtained.

(1) TiN film was oriented in the direction of (111) plane, and the diffraction pattern of TiN taken from the only TiN-coated specimen is nearly equal to that from the duplex treated specimen.

(2) The hardness measured from the specimen surface for the untreated, nitrided and TiN-coated specimens shows about $H_v\ 200$, $H_v\ 1100$ and $H_v\ 2200$, respectively. The cracks occurred in TiN film at the walls and the circumferences of the vickers-indentation traces because of the high hardness and the brittleness of TiN film. In the only TiN-coated specimen whose substrate is not nitrided, cracks are generated in TiN film with a lighter load and the number of cracks was larger because of the plastic deformation of the substrate.

(3) The wear resistance was remarkably improved by ion-nitriding, and it was improved still more by TiN-coating after nitriding. However, the only TiN-coated specimen showed the deterioration of the wear resistance inversely, because cracks were formed in TiN film under the wear condition due to the plastic deformation of the substrate and the abrasive action increased the wear loss.

(4) The nitrided stainless steels show the inferior resistance to corrosion because of the decrease of the soluble Cr due to the formation of CrN. The polarization curves tested in $0.5\ \text{kmol/m}^3\ \text{H}_2\text{SO}_4$ aq. solution indicates that the duplex treated specimens showed the decrease in the current density by about one order and the improved corrosion resistance compared with the untreated specimen, being slightly deteriorated compared with the only TiN-coated specimen.

(5) In the uniaxial fatigue test, compared with the fatigue limit of about 230 MPa for the untreated specimen, the fatigue life for the only TiN-coated specimen showed the slightly improvement and the fatigue limit for the nitrided specimen increased by about 1.5. The duplex treated specimen showed the slightly small fatigue limit compared with the nitrided specimen, but showed the increase about 1.4 compared with the untreated specimen.

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REFERENCES

- (1) M. Hudis: J. Appl. Phys., **44** (1973), 1489.
- (2) T. Takase, Y. Nakamura, M. Sumitomo, K. Kita and H. Uno: J. Japan Inst. Metals, **40** (1976), 663.
- (3) R. Urao and T. Komata: J. Metal Finish. Soc. Japan, **31** (1980), 17.
- (4) T. Bell, Z. L. Zhang, J. Lanagan and A. M. Staines: Coat. Surf. Treat. Corros. Wear Resist., (1984), 164.
- (5) Z. L. Zhang and T. Bell: Surf. Eng., **1** (1985), 131.
- (6) N. Yasumaru and K. Kamachi: J. Japan Inst. Metals, **50** (1986), 362.
- (7) F. El-Hossary, F. Mohammed, A. Hendry, D. J. Fabian and Z. Szaszne-Csih: Surf. Eng., **4** (1988), 150.
- (8) E. Angelini, A. Burdese, B. De Benedetti: Metall. Sci. Technol., **6** (1988), 33.
- (9) S.-P. Hannula, P. Nenonen and J.-P. Hirvonen: Thin Solid Films, **181** (1989), 343.
- (10) A. Szasz, D. J. Fabian, A. Hendry and Z. Szaszne-Csih: J. Appl. Phys., **66** (1989), 5598.
- (11) N. Yasumaru: J. Japan Inst. Metals, **54** (1990), 870.
- (12) K. Asami, M. Terasawa and Y. Yoshioka: Trans. Japan Soc. Mech. Eng., **42** (1976), 989.
- (13) S. Okazaki, T. Okada and H. Nakamura: J. Soc. Mater. Sci., Japan, **27** (1978), 454.
- (14) H. Imai, K. Yoshikawa and S. Imai: J. Japan Soc. for Heat Treat., **20** (1980), 13.
- (15) K. Asami: J. Soc. Mater. Sci., Japan, **31** (1982), 638.
- (16) R. F. Bunshah and A. C. Raghuram: J. Vac. Sci. Technol., **9** (1972), 1385.
- (17) E. Tsunasaawa, K. Inagaki and K. Yamanaka: J. Metal Finish. Soc. Japan, **30** (1979), 94.
- (18) E. H. Sirvio, M. S. Sulonen and H. Sundquist: Thin Solid Films, **96** (1982), 93.
- (19) A. S. Korhonen, E. H. Sirvio and M. S. Sulonen: Thin Solid Films, **107** (1983), 387.
- (20) T. Yamamoto and K. Kamachi: J. Japan Inst. Metals, **49** (1985), 120.
- (21) H. Suzuki, H. Matsubara, A. Matsuo and K. Shibuki: J. Japan Inst. Metals, **49** (1985), 773.
- (22) A. Erdemir, W. B. Carter, E. I. Meletis and R. F. Hochman: Mater. Sci. Eng., **69** (1985), 89.
- (23) A. Erdemir and R. F. Hochman: J. Mater. Energy Sys., **7** (1985), 265.
- (24) Y. Massiani, J. Crousier, L. Fedrizzi, A. Cavalleri and P. L. Bonora: Surf. Coat. Technol., **33** (1987), 309.
- (25) Y. Enomoto: J. Japan Soc. Lubrication Eng., **31** (1986), 566.
- (26) Y. Enomoto, H. Nishiyama, T. Kamoshida, A. Kaneda, K. Umeda, K. Yamanaka and H. Shimura: Reports of Mechanical Engineering Laboratory, **41** (1987), 64.
- (27) A. Wells and S. C. Yates: J. Mater. Sci., **23** (1988), 1481.
- (28) J. C. Knight, T. F. Page and I. M. Hutchings: Thin Solid Films, **177** (1989), 177.
- (29) K. Saito, A. Takei, M. Tosa, K. Yoshihara, M. Iwaki and K. Nii: J. Japan Inst. Metals, **53** (1989), 393.
- (30) K. Saito, M. Iwaki, Y. Hirohata, T. Yamashina, K. Yabe, M. Suzuki and K. Nii: J. Japan Inst. Metals, **53** (1989), 880.
- (31) D. S. Rickerby, S. J. Bull, T. Robertson and A. Hendry: Surf. Coat. Technol., **41** (1990), 63.
- (32) K. Kurokawa, T. Odaira, M. Hukushima, K. Takizawa and H. Imai: J. Surf. Finish. Soc. Japan, **41** (1990), 327.
- (33) K. Kurokawa, T. Odaira, Y. Nakayama, K. Takizawa and H. Imai: J. Surf. Finish. Soc. Japan, **41** (1990), 524.
- (34) K. Shiozawa and S. Ohshima: J. Soc. Mater. Sci., Japan, **39** (1990), 927.
- (35) K. Shiozawa and S. Ohshima: J. Soc. Mater. Sci., Japan, **39** (1990), 958.
- (36) Fatigue Data Sheet of National Research Institute for Metals, No. 33, (1983).