APPLICATION OF ION-PLATED CR-TIN MULTILAYER COATING TO STEAM TURBINE BLADES

by

Ryuichiro Ebara
Associate Chief Research Engineer
Hiroshma R & D Center
Toshihiko Odohira
Manager
Tetsuyoshi Wada
Senior Research Engineer
Advanced Technology Research Center
and
Masaaki Hatano
Associate Manager
Hiroshima Machinery Works
Mitsubishi Heavy Industries, Limited
Hiroshima, Japan

Ryuichiro Ebara is presently an Associate Chief Research Engineer at Hiroshima Research and Development Center, Mitsubishi Heavy Industries, Limited, in Hiroshima, Japan, where he has been engaged in research on structural materials since 1974. He received his B. Eng. from the Kyushu Institute of Technology and his M. Eng. and Dr. Eng. in Metallurgical Engineering from Nagoya University. Dr. Ebara has served as an Associate Professor at the Kyushu Institute of Technology and as a Post Doctoral Fellow at the University of Connecticut. He is a member of JIM, JISI, JSME, JSFSM, JWS, and ASTM (E9, E24 and G1).

Hiroshi Nakajima joined the Material Research Laboratory of Hiroshima Research and Development Center, Mitsubishi Heavy Industries, Limited, in 1982, after receiving his Bachelor of Engineering degree in Metallurgy from Osaka University. As a Research Engineer, he has been engaged in the research on evaluation of chemical plant materials.

Toshihiko Odohira is the Manager of the Advanced Technology Research Center at Mitsubishi Heavy Industries, Limited. He joined the Material Research Laboratory of Hiroshima Research and Development Center, Mitsubishi Heavy Industries, Limited, in 1962, after receiving his Bachelor of Science degree in Physics from Hiroshima University. He has been engaged in the research of evaluation of metallic and composite materials and surface treatment technique since 1962.

Tetsuyoshi Wada is a Senior Research Engineer at the Advanced Technology Research Center at Mitsubishi Heavy Industries, Limited. He joined the Material Research Laboratory of Hiroshima Research and Development Center, Mitsubishi Heavy Industries, Limited, in 1971, after receiving his Bachelor of Science degree in Physics from Hiroshima University. He has been engaged in the research of surface treatment technique, especially the PVD process, since 1971.
ABSTRACT

In order to apply a recently developed ion-plated coatings to compressor driving steam turbine blades, cavitation erosion tests were conducted to select the effective multilayer coating to prevent drain erosion of the blading material. Among the tested ion plated materials such as Cr, TiN, Cr-CrN and Cr-TiN on 13 Cr stainless steel, Cr-TiN multilayer coating showed the most effective cavitation erosion resistibility. Physical properties of the coatings were evaluated by high resolution transmission electron microscopy, scanning electron microscopy, and X-ray diffraction studies. It was determined that the high drain erosion resistibility of the Cr-TiN coating could be enhanced by a strong adhesive force at the bonded layer, high compressive residual stress of the coating, fine columnar structure, and orientation of the microstructure of the coated material.

In order to apply this coating to steam turbine blades, mechanical tests such as fatigue and corrosion fatigue, thermal shock and oxidation in steam were conducted.

It was also demonstrated that any influences of the coating were not detected on mechanical properties of the 13 Cr stainless steel.

A couple of practical application of the ion-plated coating for compressor driving steam turbine blades are briefly introduced.

INTRODUCTION

In recent petrochemical plant operations, more than five years continuous operation of condensing turbines have been required in order to maintain energy and maintenance downtime savings. The turbine blades should have the higher drain erosion resistibility to maintain their reliability.

So far, in order to prevent drain erosion of the turbine moving blades, stellite plates have been silver soldered onto the blade surface. However, silver soldering method has the following inconveniences:

- Cadmium contained in the silver solder is harmful to human body.
- The cost of silver soldering method is relatively expensive.
- A sound silver soldered joint requires very skillful manual assembly.
- Fatigue crack initiation may be initiated by a small defect of the silver soldering [1].

In order to find an effective coating to prevent drain erosion, attention was focused on titanium nitride (TiN) ceramics ion-plated coatings.

Because these coatings are well adherent to the steel substrates, and that the surface hardness of these coatings is much higher than that of the conventional coatings such as nitriding, electroplated chromium and plasma sprayed materials. Moreover, ceramics ion-plated coatings are expected to have good cavitation erosion resistibility, since the mechanical properties of the substrate are not degraded by the considerably low deposition temperature.

In this investigation, it was concluded that Cr-TiN multilayer coating had the most effective cavitation-erosion resistibility.

EXPERIMENTAL PROCEDURE

Tested Material and Ion-Plated Condition

The material used in this investigation was martensitic stainless steel (SUS410J1), austenitized at 1243K for 45 min, oil quenched, tempered at 983K for three hr, and air cooled. The chemical compositions and mechanical properties of this steel are shown in Table 1.

The coated material, its thickness, and its hardness are summarized in Table 2. Chromium, TiN and CrN coatings were deposited onto 13 Cr stainless steel by use of a hollow cathode discharge process.

### Table 1. Chemical Compositions and Mechanical Properties of the Base Metals.

<table>
<thead>
<tr>
<th>Chemical Compositions</th>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>C  Si  Mn  P  S  Ni  Cr  Mo</td>
<td>Yield Strength</td>
</tr>
<tr>
<td></td>
<td>0.2% offset,</td>
</tr>
<tr>
<td></td>
<td>Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>Elongation in 50mm,</td>
</tr>
<tr>
<td></td>
<td>Reduction of Area,</td>
</tr>
<tr>
<td></td>
<td>Charpy 2 mm</td>
</tr>
<tr>
<td></td>
<td>U Notch,</td>
</tr>
<tr>
<td></td>
<td>Impact Value,</td>
</tr>
<tr>
<td></td>
<td>N·m/cm²</td>
</tr>
<tr>
<td></td>
<td>Brinell</td>
</tr>
<tr>
<td></td>
<td>Hardness</td>
</tr>
</tbody>
</table>

- SUS410J1*: 0.13 0.38 0.49 0.022 0.003 0.49 12.10 0.36 570.3 735 27.3 68.2 262.6 217

*The material was austenitized at 1243K for 45 min. oil quenched, tempered at 983K for 3 hrs and air cooled.

### Table 2. Coating Material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (µm)</th>
<th>Hardness (HV 0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>12</td>
<td>441</td>
</tr>
<tr>
<td>TiN</td>
<td>3.5</td>
<td>1850</td>
</tr>
<tr>
<td>Cr-CrN</td>
<td>18.5 (Cr:13, CrN:5)</td>
<td>1290</td>
</tr>
<tr>
<td>Cr-TiN</td>
<td>15.5 (Cr:13, TiN:2.5)</td>
<td>1530</td>
</tr>
<tr>
<td>Stellite (Bulk)</td>
<td>—</td>
<td>593</td>
</tr>
</tbody>
</table>

The partial pressure of Nitrogen was 5.6 to 6.7 \( \times 10^{-2} \) Pa, and the total pressure of the mixed gas of nitrogen and argon was 1.1 \( \times 10^{-1} \) Pa for evaporation of titanium and chromium.

The substrate bias voltage was charged up to ~ 130 volt for Cr and TiN coatings at constant substrate temperature of 773K. The surface roughness of the base metal was 0.6 µm \( R_{max} \) for the lapped specimen, 1.6 µm \( R_{max} \), 2.4 µm \( R_{max} \) and 3.2 µm \( R_{max} \) for the polished specimen.

After the coating, conventional mechanical tests such as tensile, charpy impact, and bending tests were carried out.
Physical Properties in Microstructure Observation

X-ray diffraction analysis was carried out to determine the crystal structure, the preferred orientation, and the residual stress in the coatings. Scanning electron microscopy and high resolution transmission electron microscopy were used to observe the microstructure of the coatings.

Cavitation Erosion Test

The testing apparatus is schematically shown in Figure 1. The cavitation erosion tests were conducted based upon the ASTM Standard G32 method, by use of the specimen shown in Figure 2.

Figure 1. Ultrasonic Cavitation Erosion Testing Apparatus.

Figure 2. Cavitation Erosion Test Specimen.

The employed frequency was 18.3 kHz and the amplitude of the tip of the specimen was 40 μm. The temperature of ion-exchanged water was kept to 290K during the test.

Fatigue Tests

Rotating bending fatigue tests were conducted in air and in 3 percent NaCl aqueous solution environment. The conventional rotating bending fatigue testing machine (98 N × m) operating at 3600 rpm was employed using a specimen of the form shown in Figure 3. The fatigue tested specimens were base metal, ion-plated and eroded. The eroded specimens were prepared by blasting Al2O3 powder with average diameter of 20 μm onto the ion-plated specimen surface with rotating speed of 20 rpm.

In corrosion fatigue tests the solutions were piped to the mid-section of the specimen at a speed of 10 to 20 cm3/min.

Thermal Shock and Steam Oxidation Tests

Thermal shock tests were carried out by the heating cooling pattern as shown in Figure 4. The repeated number of cycles of the heating-cooling was ten. The rectangular plate specimen (30 × 30mm) with 5mm thickness was ion-plated and oxidized in steam environment of one atm pressure with 773K during 50 to 100 hr.

RESULTS AND DISCUSSION

Coating Structures and Its Effect on Mechanical Properties of Turbine Blading Material

The cross sectional view of a Cr-TiN ion-plated material is shown in Figure 5. The microstructure of the base metal shows a quenched and tempered martensitic structure. No degraded structures such as grain growth, were found. Defects were not found at the bonded layer among base metal, Cr and TiN coating.

Figure 3. Rotating Bending Fatigue Test Specimen.

Figure 4. Heating Cooling Pattern in Thermal Shock Test.

Figure 5. Microstructure of Cr-TiN Coated Steel.

The fracture surface of the coatings produced by the bending fracture in liquid nitrogen environment is shown in Figure 6. Both chromium and TiN coatings consist of fine columnar structure and have a sound bonded layer. The sound bonded layer was also confirmed by high resolution transmission electron microscopic observations.
It was demonstrated in the results of X-ray diffraction that the TiN and Cr coating showed (111) and (110) preferred orientation, respectively. The (111) plane of TiN (fcc) and the (110) plane of Cr (bce) are mostly closed packed crystal planes for each crystal structure.

The results of tensile, charpy impact, and bending tests did not indicate any degraded effect on the mechanical properties of the base metal. The Cr-TiN coatings showed excellent adhesion to the base metal, even after the plastic deformation as the result of the bending test.

**Cavitation-Erosion Resistibility of Cr-TiN Multilayer Coatings**

The changes of weight loss of the specimens with various kinds of coatings are shown in Figure 7. It is indicated in this figure that the weight loss of the ion-plated specimens is smaller than that of the base metal, and among the tested coatings, the Cr-TiN multilayer coating is the most effective coating against cavitation erosion.

Almost all the surface of the base metal was eroded, while the Cr-TiN coatings were not eroded over the whole surface of the specimens. Only a partial small area was eroded. The detailed observations of the eroded surface proved that the cavitation erosion frequently initiated from the small defects on the substrate originated in surface finishing process (Figure 8).

Therefore, it is anticipated that the smaller the surface roughness of the substrate, the smaller the weight loss of the coating. It has already been confirmed that the smaller the surface roughness of the substrate, the better cavitation-erosion resistibility is [2]. An improvement of cavitation erosion resistibility is also predominated by adhesive force between the base metal and coating, and residual stress in the coating [2]. It has already been clarified from the detailed microscopic observation that the cavitation erosion of TiN single layer coating initiated from the surface defect originated from the surface finishing process, and then gradually propagated through into the coatings. No disbonding between the base metal and coating was observed during the cavitation erosion process [3]. From these facts, it was surmised that the adhesive force between the base metal and TiN coating was considerably large. In the scratch test of Cr-TiN multilayer coating, it was indicated that the adhesive force increased with decreasing the surface roughness of the substrate [3].

The effect of high compressive residual stress on cavitation erosion resistibility is demonstrated in Figure 9 [3]. The cavitation erosion rate of the TiN coated specimen without heat treatment (as received) is smaller than that of the heat treated TiN coated specimen (after heat treatment) and the base metal.
The measured compressive residual stress in the Cr-TiN multilayer coating was in the range from 1700 to 2400 MPa. Cavitation erosion resistibility is also influenced by the deposition parameters in the ion plating process. In the previous work, it was confirmed that the cavitation erosion resistibility is improved by the bias voltage charge in the coating process [2].

Fatigue and Corrosion Fatigue Strength of Cr-TiN Coated Material

The results of rotating bending fatigue tests are summarized in Figure 10. The relatively small increase of fatigue strength was observed in Cr-TiN multilayer coated specimen, as compared with that of the base metal. This increase is attributed to the retardation of crack initiation of the Cr-TiN coated material, due to the compressive residual stress originated from ion-plating process.

![Figure 10. S-N curves of Cr-TiN Ion-Plated Steel in Air and in Three Percent NaCl Aqueous Solution.](image)

The influence of Al₂O₃ powder blasting on the fatigue strength was not recognized. As compared with former testing results [1], it was concluded that the fatigue strength of the Cr-TiN coated specimen was equivalent to that of TiN single layer coated specimen and was much higher than stellite soldered specimen with small cracks in the soldered layer.

Corrosion fatigue strength of Cr-TiN multilayer coated specimen is almost same as that of the base metal. The same results were obtained in corrosion fatigue tests of TiN single layer coated specimen [1]. Fracture surface observations with a scanning electron microscope revealed that corrosion fatigue cracking propagated from small corrosion pits, associating with intercrystalline fracture. The small corrosion pit was initiated at the base metal due to three percent NaCl aqueous solution transmitted throughout the small pinhole of the coating.

The same fracture surface morphology has already been confirmed in corrosion fatigue process of the 13 Cr stainless steel [4, 5]. Improvement of corrosion fatigue strength might be expected when corrosion resistant coatings without pinhole were developed. It is indicated in Figure 11 that fatigue strength of Cr-TiN coated actual blades is the same as that of the actual blades without coating.

From these results, it can be concluded that Cr-TiN multilayer coatings do not give any minor influence on fatigue and corrosion fatigue strength of the actual blades.

Influence of Thermal Shock and Steam Oxidation on Cr-TiN Multilayer Coating

The surface color of the TiN coating changed after being heated to 773K and cooled ten times. Disbonding due to the thermal shock was not found at the bonded layer between the base metal and the coating.

The weight loss due to oxidation was lower than 0.1 mg/cm³ after keeping the coated specimen in the heated steam for 100 hrs. The surface colour of the TiN coating was changed, but disbonding of the coating was not recognized.

CONCLUSION

It might be concluded through this study that the Cr-TiN multilayer coating is an effective surface treatment for improving the steam turbine blade's resistibility against drain erosion without causing a decrease in its fatigue strength, which is frequently encountered with stellite soldering.

As drain erosion behavior occurring on the turbine moving blades has not yet been formulated, it is not easy to estimate drain erosion behavior of the actual turbine blades by use of the cavitation erosion testing results. However, three years operations of compressor driving turbine in a domestic chemical company revealed that drain erosion has not yet occurred on the TiN coated last stage blades. The blade tip speed is about 300 m/sec and wetness of steam is about 10 percent.

The Cr-TiN multilayer coatings have already been applied to three compressor driving turbines in a major chemical company in the U.S.A. In addition, the laboratory investigation resulted in field data from actual turbine blades, the further development of the better drain erosion resistant coatings will be expected.

REFERENCES


ACKNOWLEDGEMENTS

The authors gratefully acknowledge Professor M. Matsumura of Hiroshima University for numerous stimulating discussions.