

# EXPOSURE TESTS OF TURBINE MATERIALS IN GEOTHERMAL STEAM FROM A DEEP PRODUCTION WELL

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## ABSTRACT

Corrosion and scaling are major problems associated with the geothermal power generation. Material tests in actual geothermal environments, along with laboratory tests, are one of the important measures to evaluate behavior of the material in relation to the corrosion and scaling problems. Since the properties of geothermal steam vary according to geothermal wells, Fuji Electric has been carrying out material tests at various geothermal wells around the world.

Recently, Fuji Electric has carried out exposure tests of the turbine materials for the period of one year, using geothermal steam from a deep production well in Japan. One of the purposes of the tests was to examine the effect of the coating to prevent scaling. Six kinds of coating materials to be applied to the blade material were selected with a thickness of approximately 200  $\mu$ m. Test specimens for corrosion tests, SCC tests and corrosion fatigue tests were installed in a test chamber and exposed to the saturated geothermal steam with the pressure of approximately 0.5 MPa. The test specimens for the corrosion tests and SCC tests were examined after 3 months, 6 months and one year of exposure, while the specimens for the corrosion fatigue tests were taken out from the test chamber after one year of exposure and were subjected to the fatigue tests in the air.

Along with the coating materials, 2 kinds of rotor materials, 2 kinds of blade materials, one kind of blade material with silver brazed stellite, and one kind of casing material were tested in the same manner as mentioned above.

After one year of exposure to the geothermal steam, 5 kinds of the coating materials revealed cracks and/or separation, while one kind of the coating material showed excellent results without any cracks or separation. Only a small amount of scaling was observed on this coating material. The test results show that this coating material is promising to be applied to the geothermal turbines.

As for the blade, rotor and casing materials, those currently used for geothermal turbines proved excellent characteristics in the geothermal steam from a deep production well.

## 1. INTRODUCTION

Geothermal power generation is a power generating system

using underground geothermal steam which, generally, has been taken from underground less than ca. 2000 m deep. However, recent utilization of so-called deep geothermal steam, geothermal steam taken from ca. 2000 to 3000 m depth, has attracted considerable attention. Utilization of deep geothermal steam has advantages, in that the amount of steam from one production well is larger and that the damage of temperature reduction given to the reservoir layer is smaller as the amount of return becomes less. At the same time, it has the disadvantage that deep geothermal steam is highly acidic and contains plenty of gaseous components such as CO<sub>2</sub> and H<sub>2</sub>S and corrosive elements such as Cl and Na—because deep geothermal steam is under high temperature and high pressure. Accordingly, Fuji Electric performed “Research and Development of a Power Generating System at the High Pressure Geothermal Steam Well Head” in collaboration with Japan Metals and Chemicals Co., Ltd. This system contains a high pressure top turbine positioned in front of a low pressure turbine to utilize the advantage of deep geothermal steam with high energy<sup>1</sup> (Figure 1). As part of this R&D, Fuji Electric carried out a series of exposure tests of the turbine materials for one year using geothermal steam from a deep production well in Japan in order to clarify the effect of the steam on corrosion behavior of the turbine materials. The tests include corrosion, stress corrosion cracking (SCC) and fatigue tests. In the tests, special attention was paid to coating materials for the purposes of protecting base material and preventing scale deposition, and these effects were investigated. Two kinds of coating, Cr<sub>3</sub>C<sub>2</sub>-NiCr and Cr<sub>3</sub>C<sub>2</sub>-FeCrAlY, were selected as anti-abrasion coating and four kinds of coating, Cr<sub>3</sub>C<sub>2</sub>-NiCr, ZrB<sub>2</sub>, CoNiCrAlY+TiN and CoNiCrAlY+Al<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub>, were selected as anti-scale deposition coating and their behaviors were evaluated by exposure tests. Anti-abrasion coatings were subjected to all corrosion, SCC and fatigue tests and anti-scale deposition coatings were subjected to corrosion test.

The geothermal steam used for the tests was the one produced from a deep geothermal steam well in Kakkonda Area in Iwate Prefecture, Japan. Depth of boring of the well was 2721 m and pressure at the well head was 7 MPa. Originally, high pressure steam is produced from the deep geothermal well; however, in tests of this time, low pressure steam depressurized to ca. 0.5 MPa was used because of restriction of test facilities. Analysis of steam condensate was also carried out (see Figure 2) and it was shown that the condensate contained relatively small amount of corrosive components and that pH was 5 to 6. Probably this was because that the steam had preferable

properties originally or that the sample analyzed was condensate from the low pressure steam. Incidentally, pH reported in the table of analysis of hot water from the same well was 4.6.

In the following, contents and results of the tests are described.

## 2. TEST PROCEDURE

Exposure to the geothermal environment was carried out for corrosion, SCC and fatigue test specimens in test facilities installed in Kakkonda Area in Iwate Prefecture for a period of twelve months maximum using deep geothermal steam of 0.5 MPa and 423 K. Materials tested were three kinds of blade materials (13% Cr steel, 13% Cr steel with stellite brazed using silver solder and Ti-6Al-4V), two kinds of turbine rotor materials (1%CrMoNiV steel and 2.5%CrMoNiV steel) and one casing material (SCPH 32 according JIS).

Corrosion tests were performed on each of the blade materials, rotor materials, a casing material and six kinds of coating materials coated on 13% Cr steel blade material. The corrosion test specimens were exposed to the geothermal environment in test facilities for periods of three, six and twelve months. Afterwards, specimens taken out of the test facilities after the specified periods were observed visually before and after pickling. After pickling, each specimen was weighed to determine the corrosion weight loss and to obtain average corrosion rate in accordance with an equation below:

$$\text{Corrosion rate(mm/year)} = \frac{\text{Corrosion weight loss(g)}}{\text{Surface area(cm}^2\text{)} \times \text{Density(g/cm}^3\text{)}} \times \frac{365}{\text{Days exposed}} \times 10$$

Subsequently, the corrosion test specimens were sectioned and examined microscopically.

SCC tests were performed on blade materials, rotor materials, a casing material and two kinds of coating materials. Each SCC specimen was stressed by a stress ring to a stress ca. 1, 0.7 or 0.5 time of 0.2% proof stress of each material and was exposed to the geothermal environment. The specimens were checked for cracking after three, six and twelve months exposure. After twelve months exposure they were sectioned longitudinally and subjected to microscopic investigation.

As for fatigue tests, tests were performed on blade materials, rotor materials, a casing material and two kinds of coating materials. Each of the fatigue specimens—after being exposed to the geothermal environment for twelve months— was subjected to reverse bending fatigue test of up to  $10^7$  cycles. Stress applied to the specimen was checked using a strain gauge fixed on surface of the specimen.

Further, fatigue test specimens not exposed were also tested for

comparison.

## 3. TEST RESULTS

### 3.1 Corrosion Test

#### Blade material

13% Cr steel specimens showed no corrosion pits (Figure 3). Corrosion rate of the specimen exposed for twelve months was ca. 0.008 mm/year (Figure 4). As for 13% Cr steel with stellite brazed using silver solder, a slight corrosion was observed in part of the silver solder. Separation of stellite due to corrosion of base metal on the boundary was observed, which had probably developed from blowholes caused during brazing. Corrosion rate of this specimen after twelve month exposure was ca. 0.007 mm/year, almost same as that of solid 13% Cr steel specimen. Ti-6Al-4V specimens had no pits and the corrosion rate after twelve months exposure was very small being less than 0.001 mm/year.

#### Rotor material

On 1%CrMoNiV steel, some deep corrosion pits were observed locally. The corrosion rate after twelve months exposure was ca. 0.004 mm/year. 2.5%CrMoNiV steel had been developed as a steel for HP-LP integral rotor for fossil-fired power plants and the specimens were taken from the LP part of the rotor. This specimen showed a few shallow pits in the surface layer. The corrosion rate after twelve months exposure was ca. 0.003 mm/year, less than that of 1%CrMoNiV steel.

#### Casing material

Casing material SCPH 32 showed deep pitting over a wide area. The corrosion rate after twelve months exposure was ca. 0.004 mm/year.

#### Coating material

$\text{Cr}_3\text{C}_2\text{-NiCr}$ , a candidate material as anti-abrasion coating, already showed cracks on the edge after three months exposure. The cracks were found to reach the base metal side of the boundary and considerable corrosion of the base metal was observed (Figure 5). Corrosion rate was ca. 0.007 mm/year. As for  $\text{Cr}_3\text{C}_2\text{-FeCrAlY}$ , separation of the surface layer of the coating was observed and its apparent corrosion rate was 0.019 mm/year, including weight loss due to separation. However, as corrosion of the base metal was scarcely observed, the substantial corrosion rate is supposed to be less than 0.01 mm/year

As for anti-scale deposition coating, only  $\text{CoNiCrAlY+Al}_2\text{O}_3 \cdot \text{TiO}_2$  showed excellent results, having only a small amount of scale deposition and moreover it showed no cracks or separation (Figure 6). The corrosion rate was also very small (less than 0.001 mm/year). Candidate coating materials other than this showed blowholes and cracks or separation, however their corrosion rates (after twelve months exposure) were less

than 0.006 mm/year and were smaller than those of uncoated 13% Cr steel specimens.

A tendency that the corrosion rate becomes smaller with progress of the exposure time was observed. This tendency is similar to that of actual erosion found on low pressure blades near the last stage, which shows a rather remarkable erosion rate in early times but a smaller rate afterwards.

### 3.2 SCC Test

#### Blade material

Though some slight pits were observed all over the surface, 13% Cr steel showed no cracks (Figure 7). The maximum depth of the pits was ca.  $30\text{ }\mu\text{m}$ . As for 13% Cr steel with stellite brazed using silver solder, slight corrosion was observed on the base metal near the edge of stellite chip. Slight pits were also observed on the base metal but cracks were not found out.

Ti-6Al-4V showed no corrosion pits nor cracks.

#### Rotor material

1%CrMoNiV steel showed corrosion pits all over the surface but no cracks were observed. The maximum pit depth was ca.  $80\text{ }\mu\text{m}$ .

2.5%CrMoNiV steel had intercrystalline cracks all over the surface and the maximum pit depth was ca.  $50\text{ }\mu\text{m}$ .

#### Casing material

SCPH 32 showed local corrosion pits but no cracks. The maximum pit depth was ca.  $85\text{ }\mu\text{m}$ .

#### Coating material

Specimens coated with  $\text{Cr}_3\text{C}_2\text{-NiCr}$ , a candidate material as anti-abrasion coating, had cracks perpendicular to the coating layer. The base material under the coating showed corrosion caused due to the geothermal steam invaded through the cracks but cracks had not observed in the base metal.  $\text{Cr}_3\text{C}_2\text{-FeCrAlY}$  specimens showed no cracks in the coating and neither corrosion nor cracks in the base metal is found.

### 3.3 Fatigue Test

#### Blade material

No pitting corrosion was observed on the 13% Cr steel specimens. Ruptured specimens, which had been highly stressed, had subcracks in the fracture surfaces. Reduction of fatigue strengths due to exposure was about 8%.

Ti-6Al-4V had showed no pitting corrosion and reduction of fatigue strength was about 6%. Subcracks were not found.

#### Rotor material

1%CrMoNiV specimens showed pitting corrosion. In all fractured specimens, subcracks were observed. Reduction of

fatigue strength was about 11%.

2.5%CrMoNiV specimens showed pitting corrosion. In all fractured specimens, subcracks were observed. Reduction of fatigue strength was about 10%.

#### Casing material

Casing material SCPH 32 had pitting corrosion. In all fractured specimens, subcracks were observed. Reduction of fatigue strength was about 12%.

#### Coating material

Specimens with  $\text{Cr}_3\text{C}_2\text{-NiCr}$  coating which showed cracks in the coating layer in the corrosion test showed separation of coating layer and base metal after fracture in the fatigue test. This occurred probably due to weakening of the adhesive strength caused by invasion of geothermal steam into the boundary where cracks had existed antecedently. Fatigue strength was lowered significantly by about 37% compared to that of base metal 13% Cr steel. In all fractured specimens, subcracks were observed.

Specimens coated with  $\text{Cr}_3\text{C}_2\text{-FeCrAlY}$  specimens showed good adhesion, though a little separation of the coating layer from the base metal was found near the final fracture surface. Subcracks were observed only in the highly stressed specimens. Fatigue strength has been increased by about 19% compared to that of the base metal (Figure 8).

## 4. CONCLUSIONS

### 4.1 Blade Material

13% Cr steel with stellite brazed using the silver solder showed separation and corrosion in part of the silver solder. They are considered to have been initiated from blowholes generated on the edge during soldering. 100% adhesion, that is, completely avoiding the separation and corrosion in the boundary layer, would be impossible in actuality because a small gap in the boundary would be caused inevitably and defects of these kinds have been observed in some tests already carried out in other geothermal fields. However, any problems have not experienced in actual use up to now.

13% Cr steel and Ti-6Al-4V showed only small corrosion rates and gave good results in corrosion, SCC and fatigue tests. 13% Cr steel now being used is proved to be enough satisfactory.

### 4.2 Rotor Material

Fatigue strength was lowered by about 10%, however lowering of such degree is considered inevitable taking into account the presence of overall corrosion and pits. Corrosion rates of both of 1%CrMoNiV steel and 2.5%CrMoNiV steel are less than 0.01 mm/year and are considered satisfactory. 2.5%CrMoNiV steel has a higher strength and a slightly better corrosion rate

than 1%CrMoNiV steel as it has a higher nickel content. However, the former steel showed intercrystalline cracks by SCC test and accordingly has a weakness for geothermal use. It was reconfirmed that the 1%CrMoNiV steel which has been used commonly is suitable for geothermal use.

#### 4.3 Casing Material

SCPH 32 showed deep pitting corrosion in both of corrosion and SCC tests, however it had no cracks and gave good corrosion rate of less than 0.01 mm/year. Reduction in fatigue strength was ca. 12%, being similar to that of rotor steel. Accordingly, this steel was considered to be suitable for casing of geothermal turbine.

#### 4.4 Coating Material

Specimens coated with  $\text{Cr}_3\text{C}_2\text{-NiCr}$ , a candidate material as anti-abrasion coating, had cracks on the edge. And it is supposed that through these cracks geothermal steam invaded into the boundary and caused separation of the coating layer from base metal and the corrosion of base metal. Cracks in the coating layer could be a cause of progress of corrosion and lowering of strength. These phenomena showed a great influence on fatigue strength. This can be understood taking into consideration that fatigue strength lowered sharply by ca. 37% compared to that of unexposed base metal though the lowering of fatigue strength of base metal itself due to exposure was only ca. 8%. Meanwhile,  $\text{Cr}_3\text{C}_2\text{-FeCrAlY}$  specimens had no cracks though they showed some separation. Consequently, invasion of geothermal steam into the base metal was only a little and fatigue strength of the specimens increased about 19% compared to that of uncoated specimens. Probably, this was mainly due to a mechanical strengthening effect of the coating layer. Thus, it was confirmed that freedom from cracks in coating layer contributed to improving the fatigue strength.

Based on the above-mentioned tests, it can be concluded that  $\text{Cr}_3\text{C}_2\text{-FeCrAlY}$  coating, one of the anti-abrasion coatings that gave good results in corrosion and SCC tests and showed a raise in fatigue strength, is one of the promising coating materials, though some problems remain in coating technology, such as separation of the coating layer.

$\text{CoNiCrAlY+Al}_2\text{O}_3 \cdot \text{TiO}_2$  coating, one of the anti-scale deposition coatings, gave the best results in corrosion test among six kinds of coating which were tested this time. Only this kind of coating showed no blowholes, cracks or separation and had only a little scale deposition. Corrosion rate was also the minimum. This time, only corrosion test was applied to  $\text{CoNiCrAlY+Al}_2\text{O}_3 \cdot \text{TiO}_2$  coating, however this material is supposed to be one of the very promising coating materials taking everything obtained in the above-mentioned tests into consideration.

Thus, some promising coating materials for future geothermal turbines could be confirmed using deep geothermal steam.

### 5. SUMMARY

Some geothermal turbine materials were tested using deep geothermal steam in Kakkonda Area in Iwate Prefecture for one year and problems anticipated before were not experienced. Materials tested showed almost the same tendency in resistance to corrosion as in previous tests and it was confirmed that corrosion rates could be estimated the same as before. Remarkable corrosion was not observed. From results of analyses on condensate, deep geothermal steam in Kakkonda Area is considered to be relatively mild. However it is possible that essential effects of deep geothermal steam might not be fully represented in the tests as the geothermal steam used for the tests had been depressurized. As a matter of course, results obtained in the tests this time cannot be applied to all the deep geothermal steam because properties of geothermal steam vary according to wells as is known. At least in the tests in Kakkonda of this time, preferable results have been obtained.

As a deep geothermal well produces high temperature and high pressure steam with high enthalpy, development of a high pressure well head power generation system, which can fully utilize the energy of the steam, will have a great advantage for the future. However, with increase in temperature and pressure of geothermal steam, effects of corrosive factors influencing the materials used will become greater. Accordingly, to realize the effective utilization of the geothermal steam, we have an intention from now on to grasp effects of deep geothermal steam on the turbine materials to resolve the remaining problems by the tests using actual high temperature and high pressure steam to establish the standard materials for deep geothermal turbines.

Further, we have an intention to carry out SCC and fatigue tests on  $\text{CoNiCrAlY+Al}_2\text{O}_3 \cdot \text{TiO}_2$  coating that showed the best results in the corrosion test and to develop better coating.

### ACKNOWLEDGMENT

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### REFERENCES

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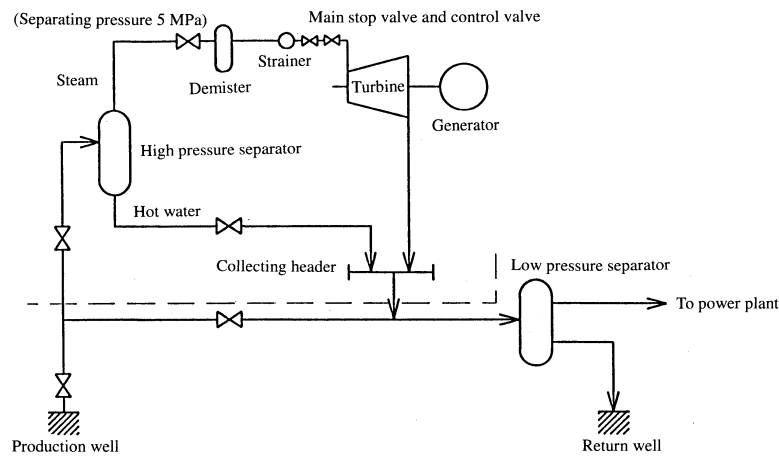


Figure 1 High Pressure Well Head Power Generation System

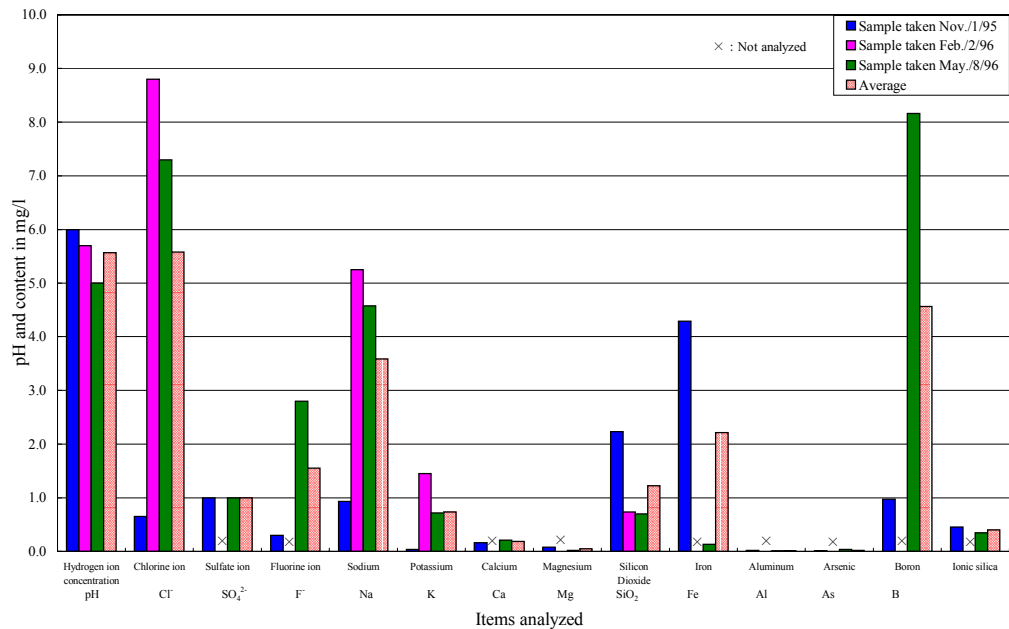


Figure 2 Result of Analysis of Condensate

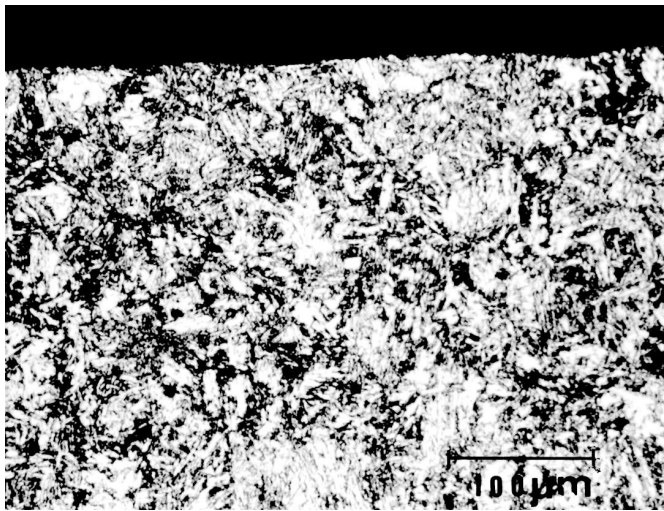


Figure 3 Microstructure of 13% Cr steel corrosion test specimen (after twelve months exposure)

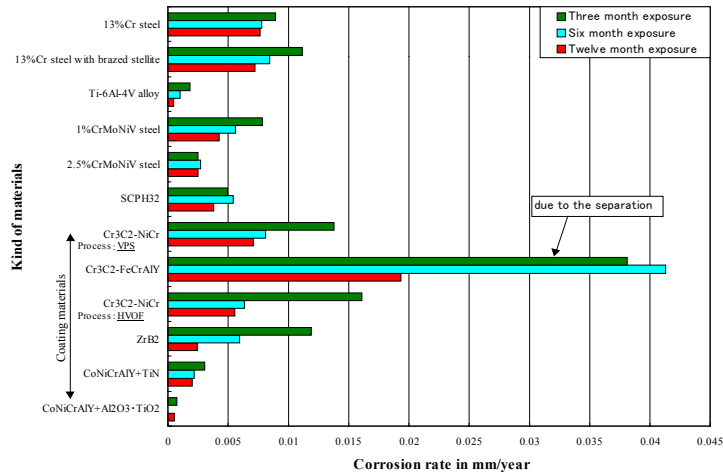


Figure 4 Comparison of Corrosion Rates of Various Corrosion Specimens

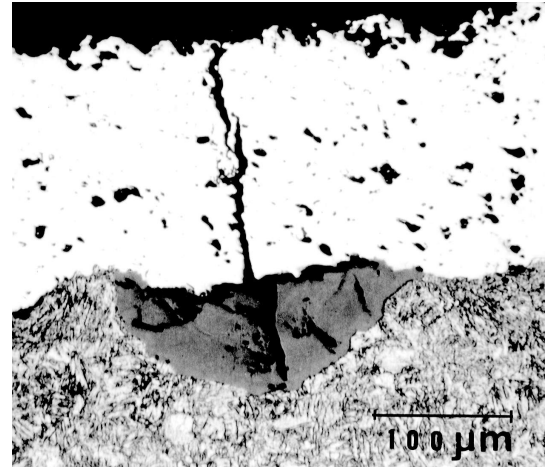


Figure 5 Microstructure of 13 % Cr steel corrosion test specimen coated with Cr<sub>3</sub>C<sub>2</sub>-NiCr (after twelve months exposure)

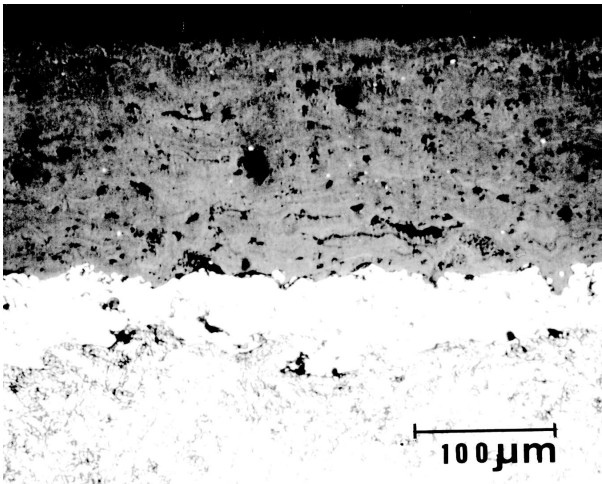


Figure 6 Microstructure of 13 % Cr steel corrosion test specimen coated with CoNiCrAlY+Al<sub>2</sub>O<sub>3</sub> · TiO<sub>2</sub> (after twelve months exposure)

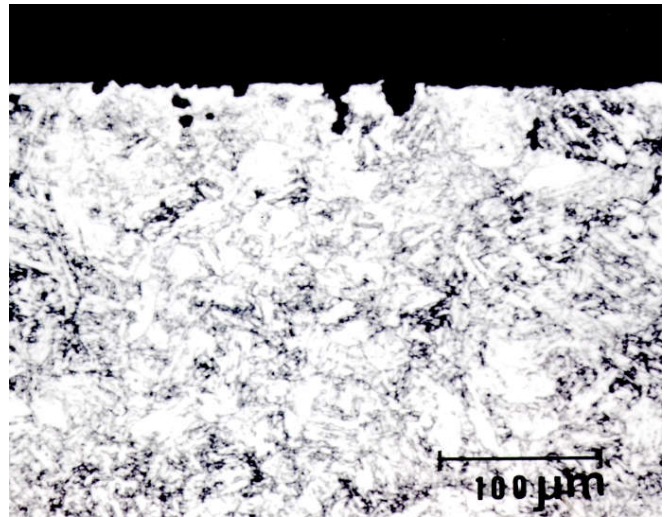


Figure 7 Microstructure of 13 % Cr steel stress corrosion cracking test (applied stress:685MPa)

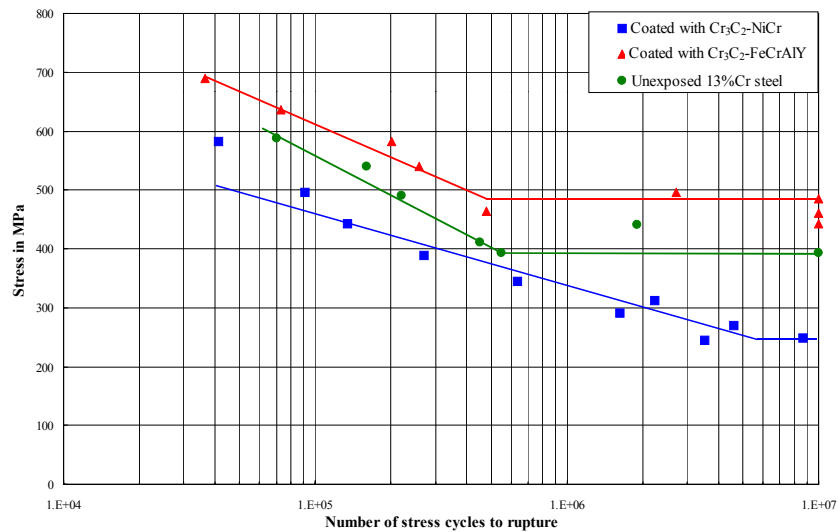


Figure 8 S-N diagram