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Corrosion and Sliding Properties of the Nickel-Based Alloys for the Valve Seats Application

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This paper describes the experiments of the corrosion and the sliding tests of the nickel-based alloys for the gate valve seating materials used at high pressure and temperature. The general corrosion rates and IGC susceptibility are tested in pressurized water at 533 K and 575 K and in Strauss test solution. The sliding tests have been done in pressurized water at 293 k, 473 K and 573 k. The alloys containing above 10% chromium may have the anti-corrosion properties that could be applied to the valve seats for the power plants. The good sliding performance and the good pressure tightness are obtained when the disc specimens that have hardness 500 to 600 Hv combined with the seat specimens that have hardness 250 to 410 Hv containing about 40 percent of iron. The large size gate valves sliding tests have certified the test results. The anti-wear properties of the seat alloy and the anti-IGC susceptibility of the disc alloy could be improved by the addition of silicon and niobium, respectively.

Keywords *: valve, power plant, nickel-based alloys, corrosion, wear, friction, leakage*

1. Introduction

Cobalt-based alloy “Stellite” is defined as CoCr-A in the American Welding Standard (AWS). The alloy is widely used as the seating materials for the valve in power plants because of the good resistance to the corrosion and erosion and the superior sliding performance. The drawbacks of Stellite are the high cost and the localization of production place of the major constituent; Co. Reducing the Co content is also important for the valve seats in the nuclear power plants because it lowers the level of radioactivity. Many efforts have been made to substitute Co by the other element such as Ni and Fe.[1)-5)] In a power plant, the greatest Co reduction would occur if the many large gate valve seats could be replaced. But the sliding performance of the replacement materials would not be as good.

The gate valves are the most widely used and they hold about 40 percent of the total valves. The valves are applied to the pipeline as to open and shut the fluid by the contact of the seats. The seats slide each other under the contact pressure forced by the fluid pressure. In the case, the moving side seat is called disc and the static side seat is called seat. And the valves are generally operated by the electric motor power. Accordingly, the anti-wear properties and the low friction coefficient are the most important factors for the seating materials of the gate valve

This study intends to develop the Ni-based alloys that do not contain Co for the gate valve seats application of power plants. The study has been carried out to clarify the corrosion properties and the sliding performance of the alloys. The sliding test was conducted using the specimens in water at high temperature (293-573 K; 8.62 MPa) under the conditions simulating the gate valve operation. The sliding performance and the pressure tightness of the large gate valves that were applied the Ni-based alloys also tested in water at high temperature (293-561 K; 7.36-9.81 MPa).

The corrosion tests have been done to certify the general corrosion rates and the IGC susceptibility in the high temperature water and in the Strauss test solution.

2. Test method

2.1 Corrosion test

The tests to certify the general corrosion rates are carried out in water at 533 K and 573 K under the pressure of 8.62 MPa. The dissolved oxygen is controlled as 2,16,19 and 31 ppm. The corrosion tests are conducted in the static autoclave for the test duration of 500 h.

2.1.1 Corrosion test materials

Fig. 1 depicts the test specimen. Table 1 tabulates the

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Table 1. Chemical composition of the corrosion test materials

Marks	Chemical composition (wt%)								Cr (wt%) Checked
	Fe	Cr	Si	C	W	B	Ni	Co	
N1*	5	17.5	6.8	0.3	1.2	0.9	Bal	-	17.4
N2	2.5	10	5.4	1	2	0.45	Bal	-	8.2
N3	7.2	19.8	6	0.3	2	0.95	Bal	-	19.3
N4	5	25	6.2		2	0.85	Bal	-	23.7
N5	5	15	5	0.3	2	0.6	Bal	-	15.5
C**	-	28	-	1	4	-	3	Bal	26.7
S	40.4	9.8	4.4	0.7	1.6	0.23	Bal	-	8.9
T***	Bal	11	-	-	-	-	0.8	-	-
M	Bal	-	0.25	0.2	-	-	-	-	-

*Sn: 0.7%, **Gas welding rod, ***Arc welding rod(Mo: 1.2%)

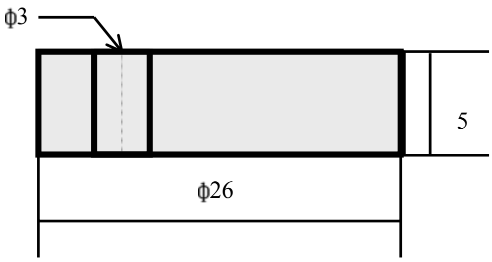

Fig. 1. Corrosion test specimen

chemical composition of the test materials.

N1~N5 and S alloys are welded to the base metals by the Plasma Transfer Arc (PTA) welding method.

C and T alloys are welded using the gas and the arc welding method, respectively.

The weld deposits of the test materials are heat-treated at 923 K and the Cr contents are checked by the chemical analysis. The test specimens are machined from the weld deposits and the surfaces are polished by # 600 paper.

2.1.2 Test conditions

Table 2 tabulates the corrosion test conditions.

Table 2. Corrosion test conditions

Items	Test 1	Test 2	Test 3	Test 4
Temperature	575K	575K	575K	533K
Dissolved oxygen (ppm)	16	19	31	2
PH	6.0	6.4	5.9	-

2.2 Sliding test of the specimens

2.2.1 Test materials and specimens

Fig. 2 depicts the geometry and dimension of disc and seat specimens. The sliding test is carried out with the combination of disc and seat specimens. Disc specimen is moving side and seat specimen is static side.

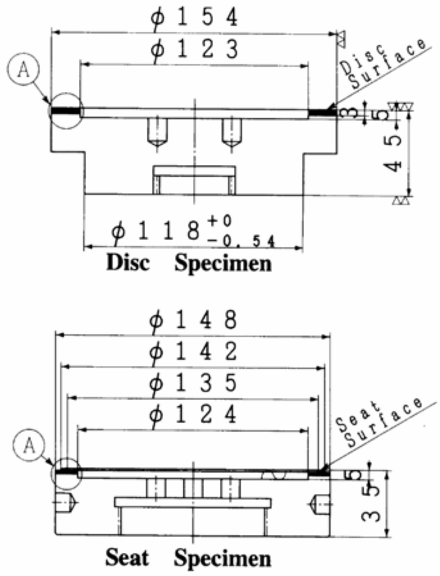

Fig. 2. Sliding test specimen

Table 3. Sliding test materials

Marks	Chemical compositions (wt %)							
	Fe	Cr	Si	C	W	B	Ni	Sn
N1	5	17.5	6.99	0.24	1.16	0.91	Bal	0.7
N2	2.5	9.9	5.34	0.97	2.11	0.50	Bal	-
S1	20.7	9.8	3.76	0.88	1.56	0.52	Bal	-
S2	40.4	9.8	4.39	0.71	1.6	0.23	Bal	-
S3	20.5	13.7	5.17	0.20	0.98	0.56	Bal	0.56
S4	35.2	10.9	4.82	0.21	0.79	0.48	Bal	0.50

Table 3 tabulates the sliding test materials. These materials are PTA powders prepared by water atomization. Disc specimens are prepared from the usual material: N1 alloy powder (in Table 3) by the PTA welding. Using N2 and S1~S4 alloys powders (in Table 3), 27 kinds of the PTA-welded seat specimens are prepared. These specimens have the different Fe contents. One set of specimens is made by Hot Iso-Static Press (HIP) to certify the sliding performance of the original N1 and N2 alloys. The raw specimens consisted of the weld deposits and the base metals are annealed at 923 K to relive the residual stress. The specimens are machined after the heat treatment. The surface of specimens are polished by the #600 paper to make the roughness less than 0.1 µmRa (the same as the service valve).

2.2.2 Test apparatus and procedure

The sliding tests for choosing seating materials are conducted with disc and seat specimens under the contact pressure of 196.2 MPa in water at temperatures of 293

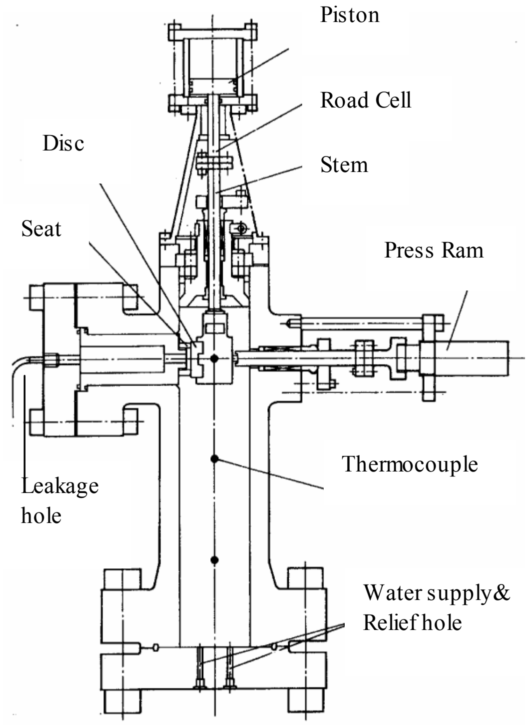

Fig. 3. Sliding test apparatus

K, 473 K and 573 K. Sliding distance is 12 mm for one cycle and sliding velocity is about 250 mm/min. The target sliding number is 100.

The test pressure, 196.2 MPa is twice the anticipated maximum pressure of 98.1 MPa applied to the valve seat (bore diameter 600 mm) when it opens at pressure difference of 7.36 MPa.

Fig. 3 depicts a schematic cross section of the test system. The fluid pressure in the vessel generates the contact pressure between disc and seat specimens like the gate valve. The sliding of disc and seat specimens are conducted by the up/down cycles of the stem connected to the sliding piston.

The friction coefficients are calculated by the reading of the load cell attached to the top of the stem. The leakages are calculated by the quantity of water leaked through the leakage hole. The arithmetic average roughness(μmRa) of disc specimens is measured by the roughness-gage for the 8 points of the circumferences of the specimens after sliding tests.

The roughness is evaluated by the average value of the 8 points and the maximum value.

The roughness of the seat specimens is not measured because the test surface widths are too narrow as 1.5 mm.

2.3 Sliding tests of the valves

The sliding tests of the valves are conducted using the 900 Lb class valves that have the 300 mm and 600 mm bore diameters in water at 293 K, 548 K and 561 K and differential pressures are 7.36-9.81 MPa.

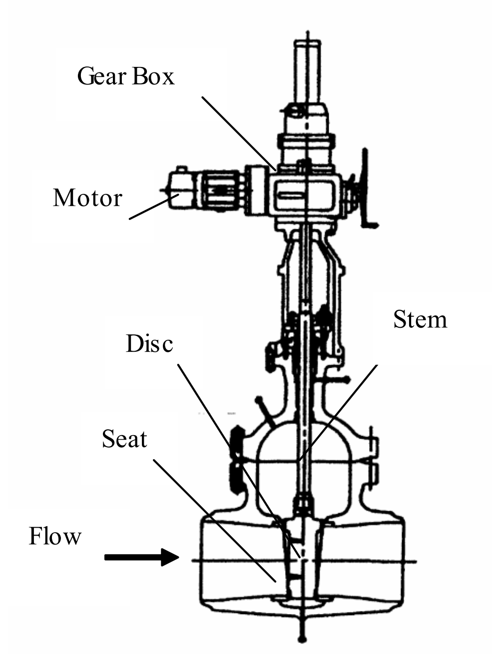

Fig. 4. Cross section of the gate valve

Table 4. Chemical composition of the modified seat materials

Marks	Chemical composition (wt %)							Si (wt%) Check	Cr (wt%) Check
	Fe	Cr	Si	C	W	B	Ni		
SP11	40.35	10.05	4.55	0.7	1.61	0.23	Bal	4.61	10.1
SP12	39.75	10.05	5.45	0.7	1.61	0.21	Bal	5.57	10.1
SP13	39.95	10.1	6.41	0.7	1.60	0.21	Bal	6.48	10.
SP14	39.85	13.1	4.44	0.69	1.51	0.23	Bal	4.57	13.3
SP15	40.35	13.1	5.41	0.7	1.60	0.21	Bal	5.31	13.2
SP16	40.35	13.05	6.39	0.69	1.59	0.22	Bal	6.45	12.9

Fig. 4 depicts the construction of the gate valve when it is shut. N1 alloy is welded to discs. N2 or S2 alloys are welded to seats.

The contact pressure is 88.3~112.8 MPa and the sliding cycles are continued to 50 or 100 cycles unless the leakages become too large to keep the inner pressure. The leakages are measured by water pressure tests under 8.62 MPa. The surface roughness of discs and seats are measured using the roughness-gauge after sliding tests.

The roughness is evaluated by the average and the maximum value of the measured values.

2.4 Modification tests

2.4.1 Modification tests of the seat material

The modification tests are conducted to certain the effect of Si and Cr contents to improve the anti-wear properties of S2 alloys (in Table 3).

Table 4 tabulates the modified seat materials. These materials are the PTA welding powders. The check analyses are run to certain Si and Cr contents of the specimens after welding. The sliding tests are conducted follow the same method mentioned in 2.2.3.

The IGC tests are conducted for SP11 and SP13 alloys by the Strauss test. These tests are run in the boiling solution of H_2SO_4 and $CuSO_4$ for 4 hours in the flask with the adverse- flow distribute condenser.

2.4.2 Modification tests of the disc material

The modification tests are conducted to improve the IGC susceptibility of the N1 alloy by the addition of Nb. Nb is added to the PTA powder as 2 to 7% using the Ni-Nb mother alloy powder. The sliding tests and the IGC tests are done to certain the effect of the addition of Nb to the sliding performance and the IGC susceptibility applied the same method mentioned in 2.4.1.

3. Test results and discussion

3.1 General corrosion rates in high temperature water

Fig. 5 shows the test results comparing with the published data in the reference.[6] The corrosion test results show the weight gain except the C and the N1 alloy (in Table 1) at the Do: 2 ppm. The results may be attributed to the oxidation of the materials. Therefore, The oxidized film thickness calculated is indicated in Fig. 5. From Fig. 5, it is clear that the thickness decrease according to the Do levels decrease and Cr contents increase.

The published data have been obtained by the test in the industrial steam at 494 K and 2.45 MPa, PH 6.8 and 0. 05 ppm and 110 PPm Do. And the steam velocity is 9 m/s. In the test, the corrosion rates of SUS304L, SES403, 21/4Cr-1Mo and Carbon steel were certified. The data show the loss of the metals. The corrosion rates decrease when the Cr contents increase. But the small differences are observed for the corrosion rates in 0. 05 ppm and 110 ppm Do.

The corrosion rate of SUS304L shows the same value of SUS403 as -0.004 mm/year when Do is 0.05 ppm.

T alloy (in Table 1) that contain 11% Cr like SUS403 is already used as the swing check valve seating material of the feed water pipeline in the fissile power plants.

The Ni -based alloys in this study contain Si and Ni and these elements would reduce the corrosion rates. Therefore, the alloys that contain above 10 %Cr may have the possibility to apply to the power plants.

This study is carried out with N1 alloy that containing 17% Cr for discs and the alloys containing 10-13% Cr for seats.

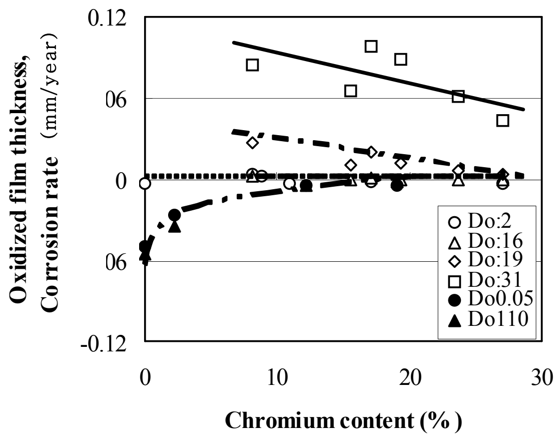

Fig. 5. Effect of chromoium contents to corrosion rates comparing with reported data

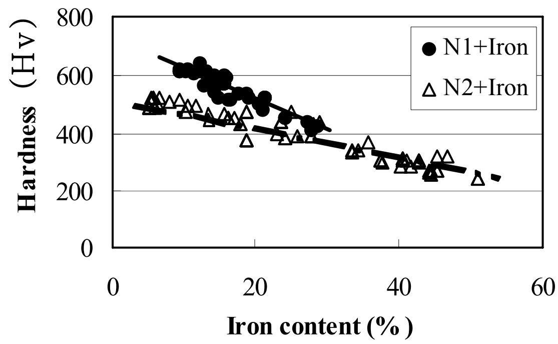

Fig. 6. Effect of iron contents to hardness of N1 and N2 alloys

3.2 Sliding tests

3.2.1 Effect of Fe contents to hardness of the alloys

Fig. 6 shows the effect of the Fe contents to Hv of N1 and N2 alloys. Hv of the alloys decrease linearly in regard to Fe contents.

The relationship between Fe contents and Hv of N1, N2 alloys are expressed by the experimental equations (1) and (2).

$$Hv = -11.6Fe\% + 753 \quad \text{for N1 alloy} \quad (1)$$

$$Hv = -6.5Fe\% + 558 \quad \text{for N2 alloy} \quad (2)$$

3.2.2 Effect of the iron contents to the surface roughness

Fig. 7 shows the relationship between Fe contents of seat and the roughness of disc specimens after the sliding tests at 293 K. From Fig. 7, two regions can be seen where the average and the maximum roughness are below 0.25 μmRa and 1 μmRa, respectively. These regions are obtained when Fe contents of seats are below 15% and above

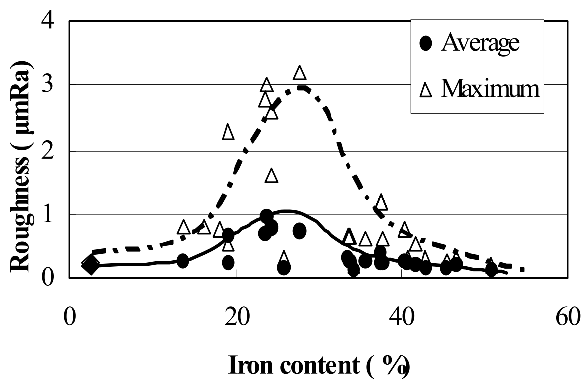

Fig. 7. Effect of iron contents to surface roughness of disc speciments (◆ ◇ : HIP)

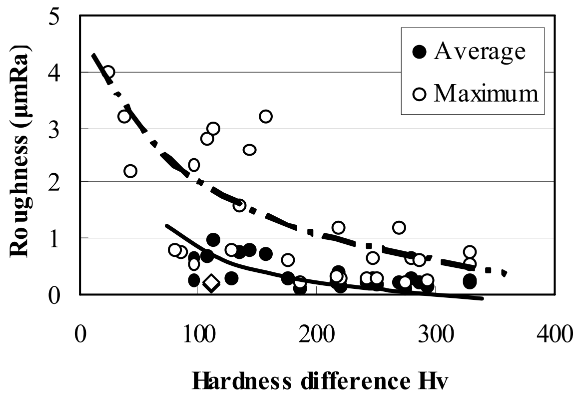

Fig. 8. Effect of hardness difference between disc and seat specimens to roughness (◆ ◇ : HIP)

35%, respectively. However, the former region is rather difficult to apply to the practical valve seats. Because, Fe contents exceed 15% frequently due to the dilution from the base metals during the welding. Accordingly, the later region is easy to apply to the practical valve seats so far as using the welding method.

The reason that Fe contents above 35% improve the sliding performance is considered as following: 1) Fe addition decreases Hv of the seat and makes the large Hv difference between disc. 2) Fe promotes the formation of an oxide film ($NiFe_2O_4$: Trevorite) that works as the lubricant. In 573 K tests, the test results show the good sliding performance in regard to whole Fe contents from 2.5 to 50.9%. Because, the combinations of specimens that indicate the good sliding performance at 293 K are tested at 573 K. The roughness of disc tested at 573 K is that the average values are 0.4 - 0.7 μmRa and the maximum values are 0.7 - 1.2 μmRa.

Fig. 8 shows the effects of Hv differences between disc and seat specimens to the roughness of disc at 293 K.

It is well known that Hv differences are the important factor to insure the good sliding performance. The lower Hv material could not hurt the higher Hv material under the large Hv difference. The inclinations of the data in Fig. 8 match the general theory. However, the relationship between Fe contents and the sliding performance are rather important to develop the good sliding performance alloys, because Fe contents are directly control the properties.

3.2.3 Leakage of the specimens and valves

Fig. 9 shows the relationship between Fe contents and the leakages of the specimens and the valves. The low leakage regions are corresponded to the fine roughness regions. The small size specimens show the similar leakage values of the large-scale valves when the leakages are evaluated using the unit of ml/25 mm/3.6 ks. Fig. 10 shows the roughness and the leakages of the valves tested at 293 K, 548 K and 561 K. The leakages of the valves are limited to 2 ml/25 mm/3.6 ks when the valves are newly produced. From Fig. 10, it is found that the leakages of the valve are about 1 ml/25 mm/3.6 ks after sliding tests at room temperature and the order of magnitude of 10 ml/25 mm/3.6 ks after sliding tests at high temperatures.

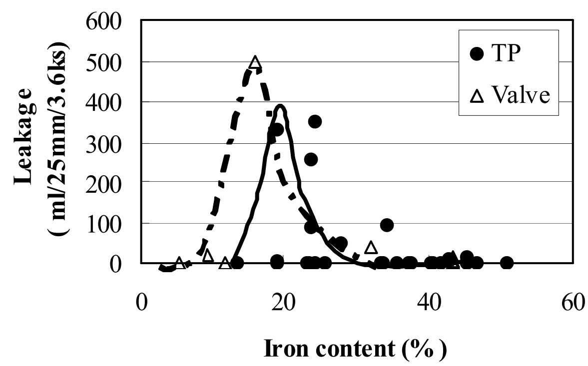

Fig. 9. Realtionship between iron contents and water leakage of specimens and valves

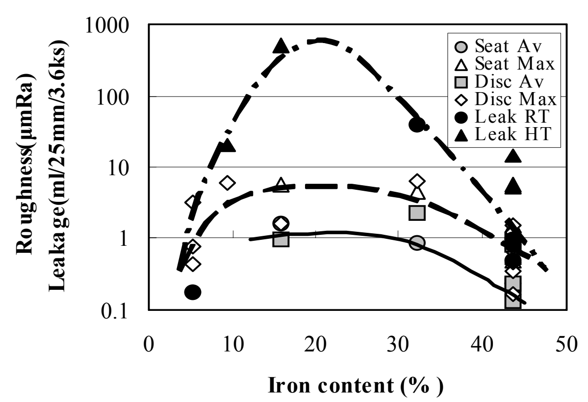

Fig. 10. Realtionship between iron contents and roughness and leakage of valves

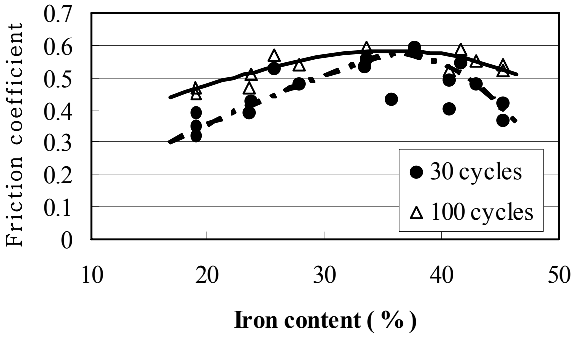

Fig. 11. Effect of iron contents to friction coefficients

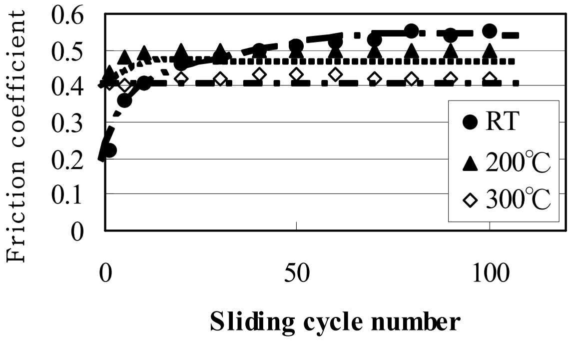

Fig. 13. Friction coefficient of N1 and S alloys in relation to sliding cycles

3.2.4 Friction coefficients

Fig. 11 shows the relationship between Fe contents and the friction coefficients of the specimens tested at 293 K.

The friction coefficients are generally larger at room temperature than at high temperatures. From Fig. 11, it is found that the coefficients are related to Fe contents. And the values increase to 0.6 when Fe contents increase to 35% after 100 cycles. However, the values decrease to 0.5 levels when Fe contents increase to 45%. The value of 0.5 is generally applied to the design of the gate valve. The relationship between Fe contents and the friction coefficient are expressed by the experimental equation (3).

$$\mu = 0.3\sigma R^{1/4}/Hv \quad (3)$$

Where,

μ: Friction coefficient

σ: Tensile strength as $\sigma = 986 - 6Fe\%$, (MPa)

R: Average roughness reading from Fig. 7, (μmRa)

Hv: Hardness determined by equation (2), (Hv)

The equation indicates that the friction coefficients are related to the strength and the hardness of the soft side materials and disc roughness. (Disc and seat may have the similar roughness). Fig. 12 shows the relationship between Hv differences and the friction coefficients. From Fig. 12, it is found that the coefficients increase according to Hv differences increase. And the value reaches to 0.6 at the difference of 270 Hv. But it does do not increase beyond 0.6 in spite of the differences are above 270 Hv.

Fig. 13 show the changes of the friction coefficients during the sliding tests up to 100 cycles at 293 K, 473 K and 573 K.

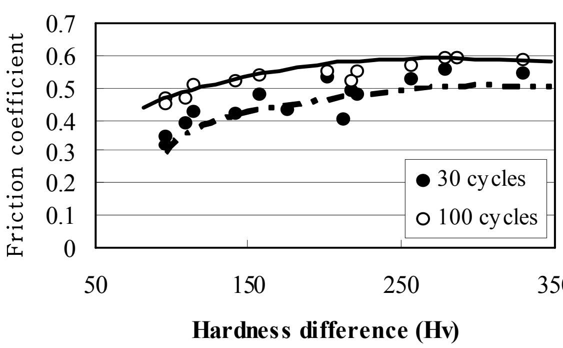

Fig. 12. Effect of hardness differences to friction coefficients

3.3 Modification test results

3.3.1 Modification tests for seat material

Fig. 14 shows the effects of Si contents to Hv of SP alloys (in Table 4). Hv of the alloys changes from 315 to 410 Hv when the Si contents increase from 4.5 to 6.5%. Hv of the alloys containing 13%Cr are smaller about 35 Hv than Hv of the alloys containing 10%Cr.

The IGC are observed for the alloys tested in the Strauss test solution. The IGC are occurred uniformly around the fine austenite grains so that the SCC may not occur to the SP alloys. Fig. 15 illustrates the roughness of disc specimens tested at 293 K and 573 K. The roughness becomes so fine when the Si contents of seat increase to 6.5%.

Therefore, Si addition to seat could improve the anti-wear properties of disc and seat. But the friction coefficients increase to 0.55 at 293 K before the 100 cycles sliding when the alloys contain 13% Cr and 5.5 - 6.5% Si

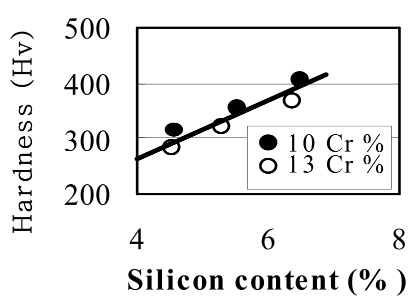

Fig. 14. Effect of silicon contents to hardness

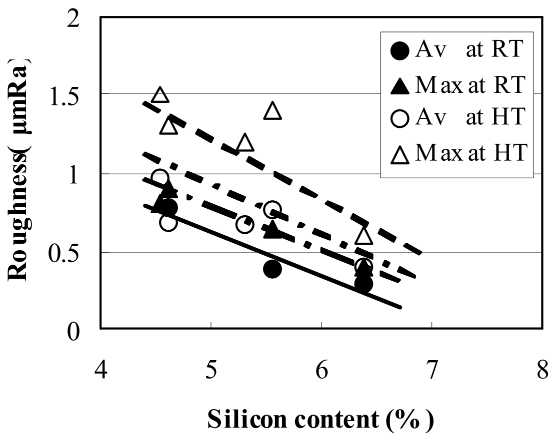

Fig. 15. Effect of silicon contents to surface roughness of disc specimens

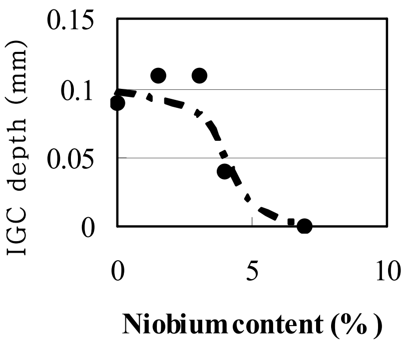

Fig. 16. Effect of niobium addition to IGC of N1 alloy

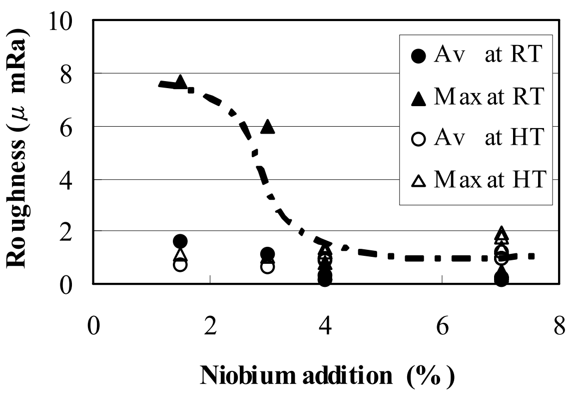

Fig. 17. Effect of niobium addition to surface roughness of N1 alloy disc

3.3.2 Modification tests for disc material

Fig. 16 indicates the effect of the addition of Nb to the IGC properties of the N1 alloy. From Fig. 16, it is found that the depth of the IGC decreases when Nb addition is 4% and that it becomes zero level when the addition is 7%. Accordingly, Nb is considered to improve the IGC properties of the N1alloy.

Fig. 17 shows the roughness of discs of N1 alloy containing Nb tested at 293 K and 573 K. The large roughness values are observed at 293 K test when the alloy contains 1.5 and 3% Nb. But the fine roughness is obtained when the Nb contents are 4 and 7%. The friction coefficients increase to 0.55 before 100 cycles sliding when the alloys contain 4 and 7% Nb at 293 K.

4. Conclusions

1) Nickel-based alloys containing above 10% chromium may have the anti-corrosion properties that could be applied to the valve seats for the power plants.

2) The combinations of disc alloys that have hardness of 500 to 600 Hv and seat alloys that have hardness of 250 to 410 Hv containing about 40% iron show the good sliding performance and the good pressure tightness in the room and high temperature pressurized water.

The tests using the valves certify the applicability of the combination as the gate valve seats.

3) The silicon modifies the anti-wear properties of the seat alloy and the niobium improves the anti-IGC properties of the disc alloy.

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