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Controls of chromium and third element contents in nickel-base alloys for corrosion resistant alloys in hot HNO_3–HF mixtures

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ABSTRACT

Corrosion resistances of nickel-base alloys in HNO_3–HF mixtures were investigated to apply them to FLUOREX process, which is advanced hybrid process of fluoride volatility and solvent extraction for next-generation spent nuclear oxide fuel reprocessing. Many types of Ni–Cr and Ni–Cr–X (X = Mo, W, Nb, Ti, Si, Cu) ingots were experimentally manufactured and the desirable chromium and third element contents in nickel-base alloys were discussed in narrow range to improve the corrosion resistance in hot HNO_3–HF mixtures. From the results of corrosion tests, Ni–45Cr–0.25Mo alloy exhibited the best corrosion resistance in this study. The corrosion rate was 0.17 mm/y in 8 M HNO_3–0.1 M HF solutions at 373 K and it provided good performance as corrosion resistant materials. In conclusion, the controls of higher chromium content and a small amount of molybdenum in nickel-base alloys are significant to improve the corrosion resistance in HNO_3–HF mixtures condition for the FLUOREX process.

1. Introduction

FLUOREX (Hybrid Process of *Fluor*ide Volatility and Solvent *Ex*traction) process has been proposed as one of the next-generation advanced reprocessing methods to adapt to transition period from light water reactors cycle to fast breeder reactors cycle [1–3]. The process is constructed from uranium removal from spent nuclear fuel by fluoride volatility method and aqueous reprocessing of residual fuels by solvent extraction method. The application of fluoride volatility method on spent nuclear fuel reprocessing has great advantage for the transition period because the uranium removal ratio in the fluoride volatility method can be controlled by fluorine flow ratio [3], therefore, the latter solvent extraction method in the FLUOREX process can consistently accept residual fuels of similar U/Pu ratio owing to the control of uranium removal. In this way, as useful option for next-generation reprocessing method, the FLUOREX process has flexibility to accept various burn-up types of spent nuclear fuel generated in the transition period.

However, there are still some technical subjects in the FLUOREX process [1]. One of the subjects includes an interface issue between the fluoride volatility and the solvent extraction methods. Fig. 1 shows the flow of FLUOREX process. The procedure of the FLUOREX process is described as follows. The supplied spent nuclear oxide fuels are sheared and pulverized by dry decladding method. The pulverized fuels are supplied into flame tower reactor and fluorinated by purified fluorine gas under high temperature condition. About 90 wt% of the uranium is removed from the spent fuel as volatile uranium hexafluoride (UF_6) by the fluorination. The volatile UF_6 is purified by passing through some absorbents such as sodium and magnesium fluorides, so the decontamination factor (DF) of the recovery uranium can be improved to about 10^7 by the purification system. About 10 wt% residue including plutonium, residual uranium, and fission products are converted to oxides and then dissolved into nitric acid solution for solvent extraction process. However, it is technically difficult to convert the all of fluorides in the residue to oxide, so the FLUOREX process must accept the contamination of some fluorides in the nitric acid solution. The contamination gives a strong impact on a corrosion of equipment materials in solvent extraction method.

Generally, the choices of engineering alloys to handle HNO_3–HF mixtures are very limited owing to the strong corrosive solution. Several types of austenitic stainless steels are widely used as equipment materials in worldwide industrial PUREX plants [4–7]. They exhibit good corrosion resistance in hot nitric acid solutions owing to their passivity, which results from the formation of oxide films [8–10]. However, in the presence of fluoride ions in nitric acid solutions, the corrosion rates of stainless steels are greatly increased [11–13]. It is actually known the HNO_3–HF mixtures are typically employed in pickling of stainless steels. In this study, the nickel-base alloys were focused to find the corrosion resistant materials for aqueous reprocessing in the FLUOREX process.

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Table 1
Chemical composition of commercial alloys.

Materials	Chemical composition (wt%)												
	C	Si	P	s	Cr	Mn	Fe	Ni	Mo	Cu	Co	W	V
SUS304L	0.025	0.62	0.024	0.008	18.25	1.22	Bal.	9.11	–	–	–	–	–
Inconel 690	0.02	0.12	0.004	0.001	29.68	0.26	10.1	Bal.	–	–	–	–	–
Monel 400	0.1	0.1	–	<0.002	–	1.1	–	Bal.	–	32	–	–	–
Hastelloy C-276	0.004	0.07	<0.001	<0.001	16.4	0.5	5.7	Bal.	15.7	–	1.7	3.6	0.01
MC-alloy	0.004	0.07	<0.001	<0.001	44.4	0.19	0.14	Bal.	0.96	–	–	–	–

This corrosion study is consisted of the following four steps. The first step is a corrosion survey of commercial alloys including four types of nickel-base alloys and a stainless steel. In the second step, the desirable chromium content in nickel-base alloys was discussed to improve the corrosion resistance in HNO_3–HF mixtures. Furthermore, the effects of third element addition and molybdenum content in Ni–Cr alloys on corrosion resistance were discussed in third and final steps, respectively. This paper describes the results of desirable composition control based on nickel alloys for corrosion resistant materials in hot HNO_3–HF mixtures.

2. Experimental

2.1. Steps of corrosion study

Five types of commercial alloys with various chemical compositions, SUS304L, Inconel 690, Monel 400, Hastelloy C-276, MC alloy, were selected in the first step. The MC alloy, a corrosion resistant wrought alloy with improved corrosion resistance to HNO_3–HF mixtures, was regarded as a standard of corrosion resistant materials in this study. In this step, the relationship between the chemical compositions in the alloys and the corrosion rates was discussed to find the beneficial elements on improving the corrosion resistance in HNO_3–HF mixtures. The chemical compositions of the commercial alloys are given in Table 1. Next, the desirable chromium content in nickel-base alloys was discussed in the second step. The chromium effect in nickel-base alloys for the improvement of corrosion resistance in HNO_3–HF mixtures was pointed out in previous corrosion studies [14–19]. We investigated the corrosion behavior of Ni–Cr alloys around 46 wt%Cr in HNO_3–HF mixtures referring to the previous corrosion data. Horn et al. investigated the effect of chromium content on corrosion resistance of nickel-base alloys in hot HNO_3–HF mixtures [14]. In their study, the wide range from 20 wt%Cr in nickel-base alloys to pure chromium was covered to evaluate the effect of chromium content on corrosion rate in HNO_3–HF mixtures. The results showed the corrosion resistance was greatly improved with the increase of chromium content in the range of less than 46 wt%, on the other hand, the chromium effect was not significant in the range of more than 46 wt%. Accordingly, we studied that the effect of chromium content in narrow range around 46Cr wt% on the corrosion resistance was evaluated to find the most desirable chromium content in nickel-base alloys. In the third step, the effect of third element addition with a small amount was discussed to improve the corrosion resistance of the selected Ni–Cr alloy from the second step. We selected molybdenum, tungsten, niobium, titanium, silicon and copper as the candidates of the third element. The molybdenum and tungsten are commonly pointed out as the beneficial elements to improve the corrosion resistance in non-oxidizing acids such as hydrofluoric acid [15–17]. As for the niobium and titanium, we expected the improvement of corrosion resistance owing to oxide films as well as the behavior in pure nitric acid solution. The copper and silicon were selected because they improve the resistance of nickel to non-oxidizing acids [20–21]. Ni–Cu alloys such as Monel 400 are commonly used in pure HF solution from the viewpoint of corrosion resistance [22]. The additive ratio of the third element in the Ni–Cr alloys was consistently adjusted to 0.5 wt% not to disturb the chromium effect. In the final step, the effect of molybdenum content in Ni–Cr alloys was discussed because it improves corrosion resistance to non-oxidizing acid such as hydrofluoric acid. The desirable composition for corrosion resistant nickel-base alloys in HNO_3–HF mixtures was discussed through such four steps.

2.2. Alloy preparation

Many types of the experimental Ni–Cr alloys such as Ni–αCr (α = 43, 45, 46, 47, 49 wt%), Ni–Cr–0.5 wt%X (X = Mo, W, Nb, Ti, Si and Cu) and Ni–Cr–βMo (β = 0.1, 0.25 wt%) were prepared for the corrosion tests in this study. The alloy preparation procedure is given in Fig. 2. First of all, the elemental powders of pure metals (more than 99.9%, respectively) were melted by argon arc method to get about 200 g of button ingots. Fig. 3 shows the appearance of the Ni–αCr button ingots. Subsequently, the ingots were homogenized at 1503 K for 10 h under vacuum condition to remove heterogeneous structure in the ingot. The sheets in thickness of 2 mm were prepared by hot roll process at 1503 K for 10 h to decompose the solidification structures such as crystallization and dendrite. They were finally annealed at 1453 K for 30 min to make a better solid solution. Fig. 4 shows appearance of Ni–αCr alloys after the hot rolling and the annealing. Some big cracks were observed on the surface of Ni–49Cr alloy and a lot of tiny cracks were observed at edge of Ni–47Cr alloy sheet. Thus, the fabricability of alloy sheets more than 47 wt%Cr became worse. The alloy sheets with no cracks were given in case of less than 45 wt%Cr. In relation to the effect of the chromium content in Ni–Cr alloys on the mechanical properties, *Sugahara* pointed out Cr-alpha phase ratio increases in case of chromium content beyond 45 wt% and it results from the extreme drop of elongation [17].

2.3. Test conditions

All of the samples for the corrosion tests including some commercial alloys were finally cut into sizes of 10 mm × 10 mm in thickness of 2 mm. The samples were polished by SiC paper to 400 grit and cleaned ultrasonically in acetone. Fig. 5 shows schematic of corrosion test apparatus. The corrosion tests were performed in some Teflon pots to prevent the attack from fluoride ions and a pot was connected with water-cooled condenser through a tube. The condenser and tube were also made of Teflon. All of the samples were immersed in 8 M HNO_3–0.1 M HF solutions at

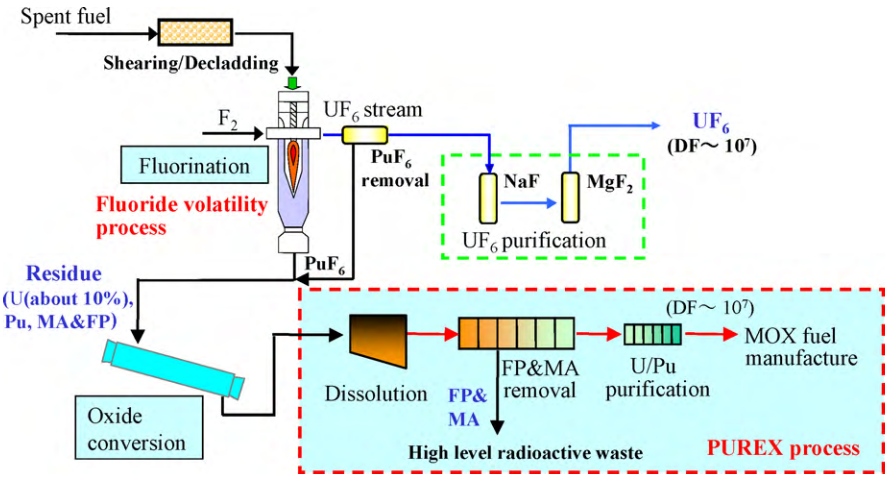


Fig. 1. Process flow of FLUOREX.

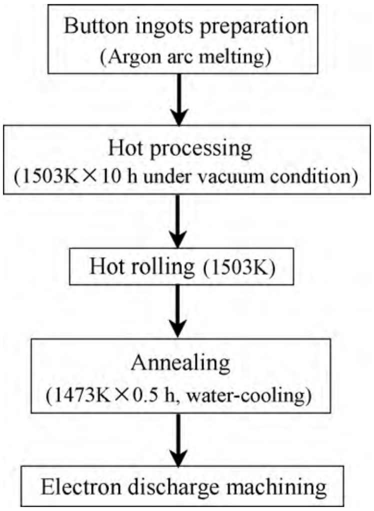


Fig. 2. Procedure of alloy preparation.

373 K. The different kinds of samples were not simultaneously immersed in a pot. The composition of the test solution was decided based on provisional concentrations of nitric acid after spent fuel dissolution and fluoride ion carried from oxide conversion stage in the FLUOREX process. The test solution was controlled in oil bath at 373 K. Half a liter of the test solutions was prepared for every batch. The ratio of solution volume to surface area of sample was approximately 60 ml/cm^2. Two samples of the same kind of alloys were put on the exclusive rack in a pot and immersed in the test solution for 100 h without renewing the test solution. After the corrosion test was finished, the samples were picked up from the pot and washed by distilled water and acetone. The samples were completely dried and the weight loss was measured to calculate the corrosion rate according to the following equation. In addition, the microstructures on material surfaces were observed by scanning electron microscope (SEM) or optical microscope (OM) to acquire the information of corrosion state. In the first step, the chemical compositions on surface of the corroded commercial alloys were analyzed by Electron Probe Micro Analyzer (EPMA).

$$\text{Corrosion rate (mm/y)} = \frac{(\Delta M \times 10^3 \times 365.25 \times 24)}{(S \times t \times d)} \qquad (1)$$

ΔM, weight loss (g); S, surface area (mm^2); t, immersion time (h); and d, density of sample (g/cm^3).

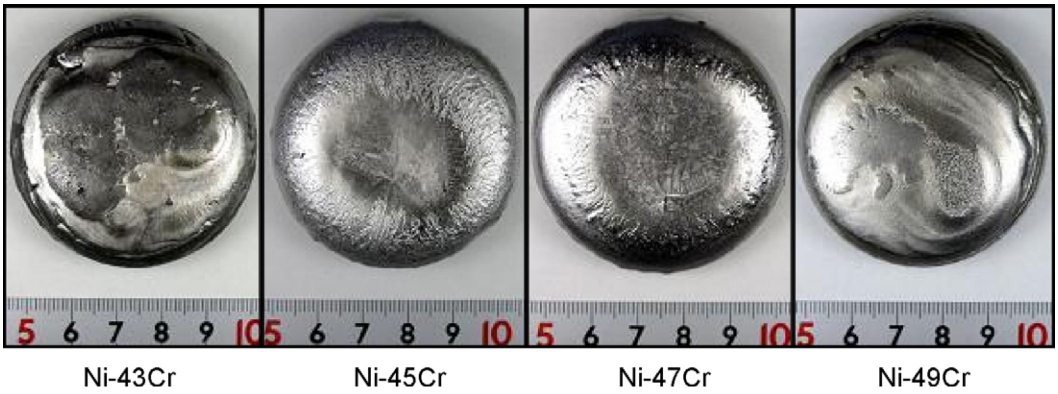


Fig. 3. Schematic of corrosion test apparatus.

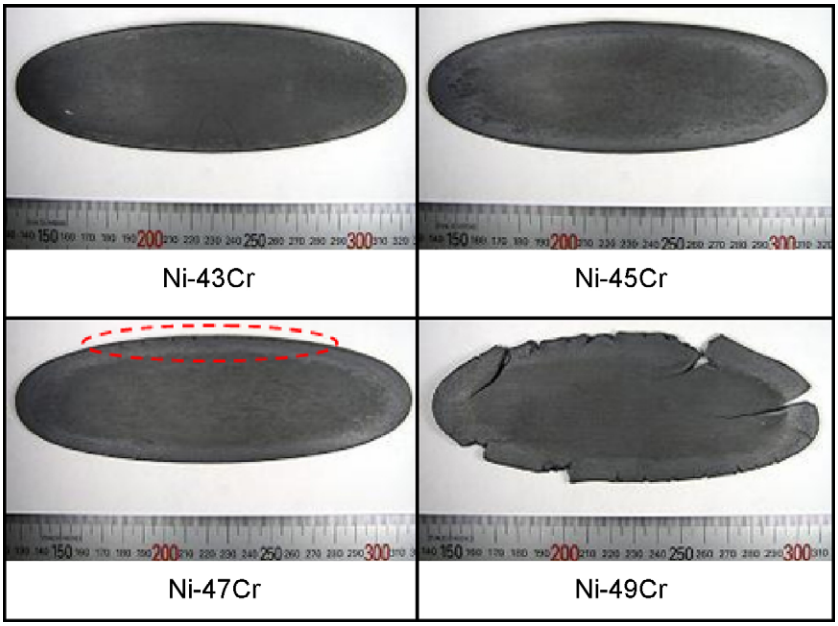


Fig. 4. Button ingots of Ni–Cr alloys.

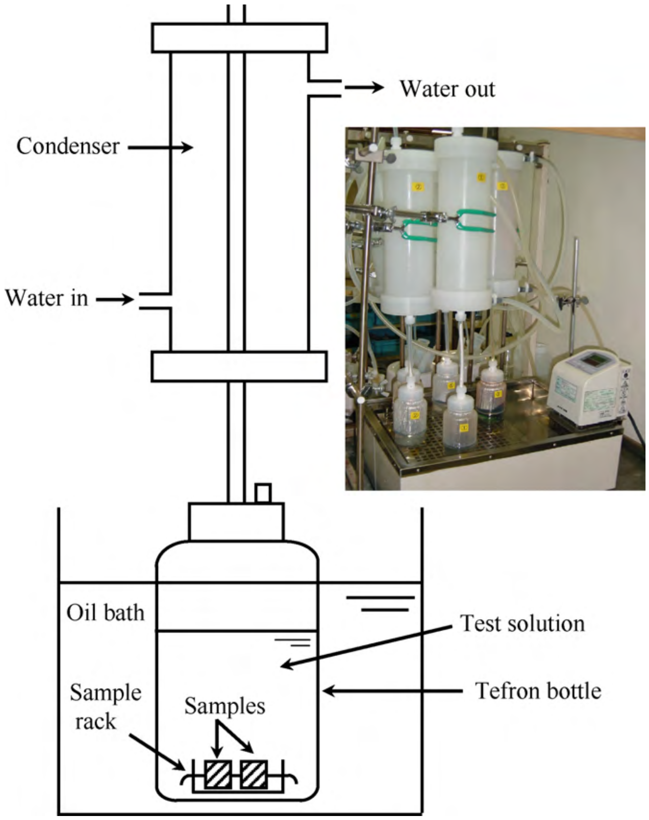


Fig. 5. Appearance of Ni–Cr alloys after hot rolling.

3. Results and discussion

3.1. Corrosion behavior of several commercial alloys in HNO_3–HF mixtures

Fig. 6 shows the corrosion rates of several commercial alloys in 8 M HNO_3–0.1 M HF solutions at 373 K. Only Monel 400 samples were completely dissolved during the corrosion test, so the minimum corrosion rate of Monel 400 was shown in the figure by supposing all of the initial sample weight as weight loss for 100 h. In the selected commercial alloys, the MC alloy exhibits the best corrosion resistance in the hot HNO_3–HF mixtures. Fig. 7 shows the effect of chromium content in the commercial alloys on the corrosion rate. The corrosion resistance is improved with the increase of chromium content in the alloys and the chromium is a beneficial element to improve the corrosion resistance in HNO_3–HF mixtures.

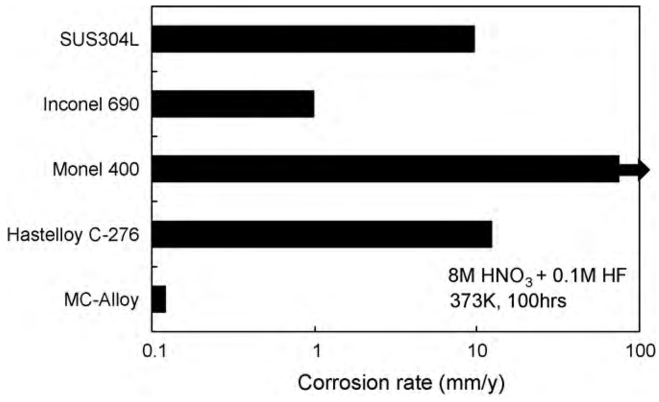


Fig. 6. Corrosion rates of commercial alloys.

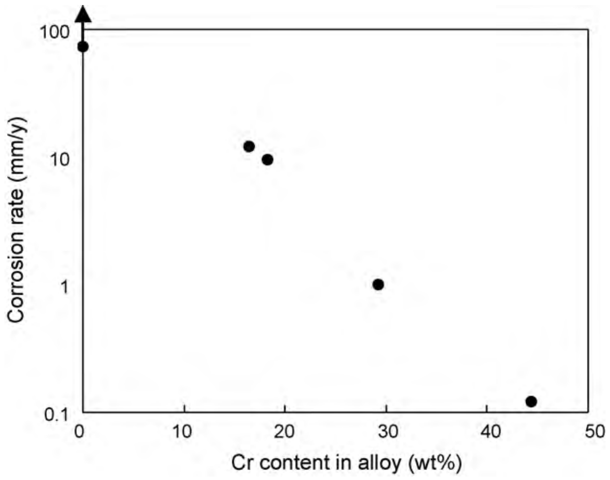


Fig. 7. SEM morphologies of commercial alloys.

So, in the next step, the desirable chromium content in Ni–Cr alloy was discussed. There was no likely relationship between other elements and the corrosion rate. Fig. 8 shows SEM morphologies of SUS304L, Hastelloy C-276, Inconel 690 and MC alloy. The surfaces of Hastelloy C-276 and Inconel 690 included a lot of pitting, on the other hand, there were no corrosion tracks on the MC alloy surface. The SUS304L showed the resistance to pitting in this condition however the corrosion rate was relatively high. Fig. 9 shows EPMA analysis results for the alloy surfaces. The surface compositions on the corroded samples of SUS304L and Inconel 690 were no change in comparison with that of fresh samples. In the MC alloy and Hastelloy C-276, however, only molybdenum was slightly concentrated on the surface by the corrosion phenomena. It must be related to beneficial element in HNO_3–HF mixtures.

3.2. Effect of chromium content in Ni–Cr alloys

As the second step, the effect of chromium content in nickel-base alloy on corrosion resistance in HNO_3–HF mixtures was discussed in the narrow range of 43–47 wt%Cr referring to Horn's study [14]. In the corrosion study, several kinds of Ni–Cr alloys including minor element such as iron and molybdenum were prepared to discuss the chromium content effect, but we used pure Ni–Cr alloys to prevent the corrosion effect from minor elements. Fig. 10 shows the effect of chromium content in Ni–Cr alloys on corrosion rate in 8 M HNO_3–0.1 M HF solutions at 373 K. From the results, the adding of chromium content more than 45 wt% did not affect the improvement the corrosion resistance. Additionally, as shown in Fig. 4, the fabricability of Ni–Cr alloy got worse owing to the excess of chromium content. It is a fact that no commercial nickel-base alloys exceed 45 wt%Cr are available. Thus, the most desirable chromium content for corrosion resistant Ni–Cr alloys in HNO_3–HF mixtures was decided as 45 wt% in this study, hence the Ni–45Cr alloys were consistently used for the third and final steps.

3.3. Effect of third element addition in Ni–45Cr alloys

In the third step, the effect of third element addition was discussed to improve the corrosion resistance of the pure Ni–45Cr alloy in HNO_3–HF mixtures. Samples of Ni–45Cr–0.5X (X = Mo, W, Nb, Ti, Si, Cu) alloys were prepared for corrosion test. The fabricability of these alloys included no problems as the cases of Ni–47Cr and Ni–49Cr alloys. Fig. 11 shows the corrosion rates of Ni–45Cr–0.5X alloys in 8 M HNO_3–0.1 M HF solutions at 373 K. The Ni–45Cr–0.5W alloy exhibited the best corrosion resistance in the selected alloys

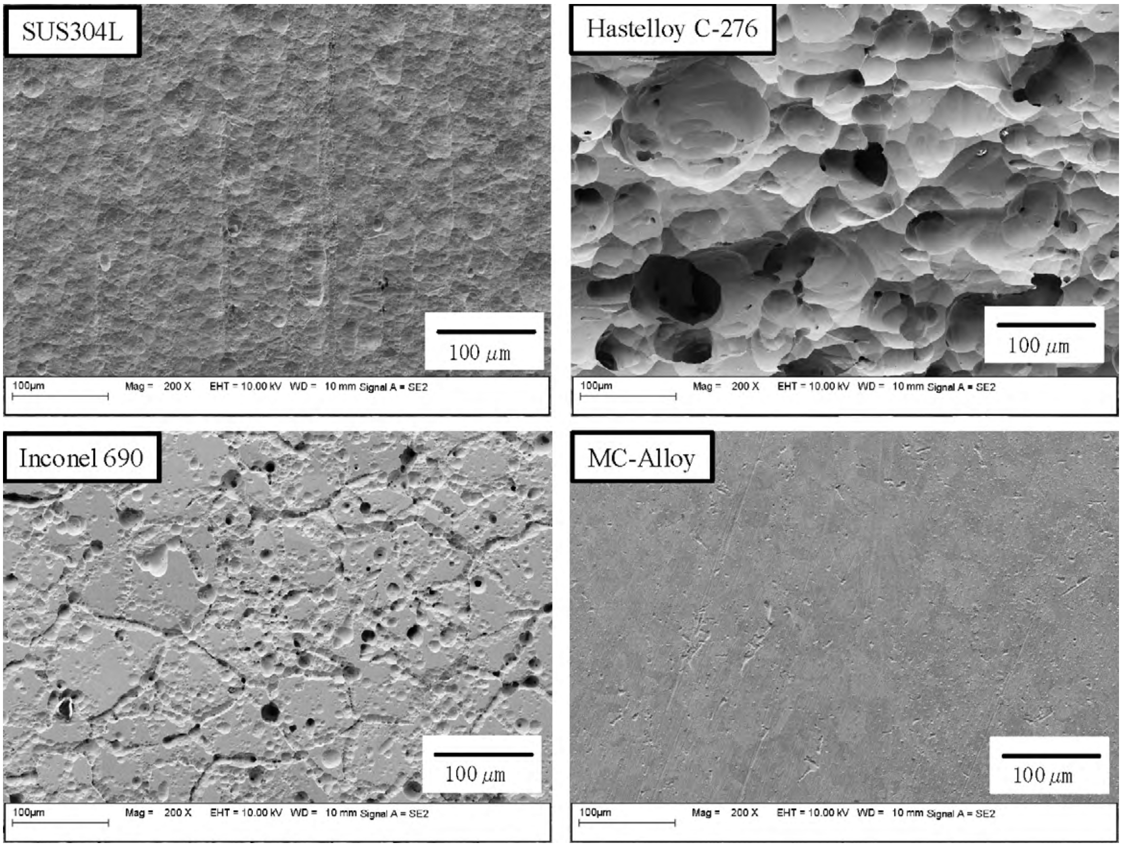
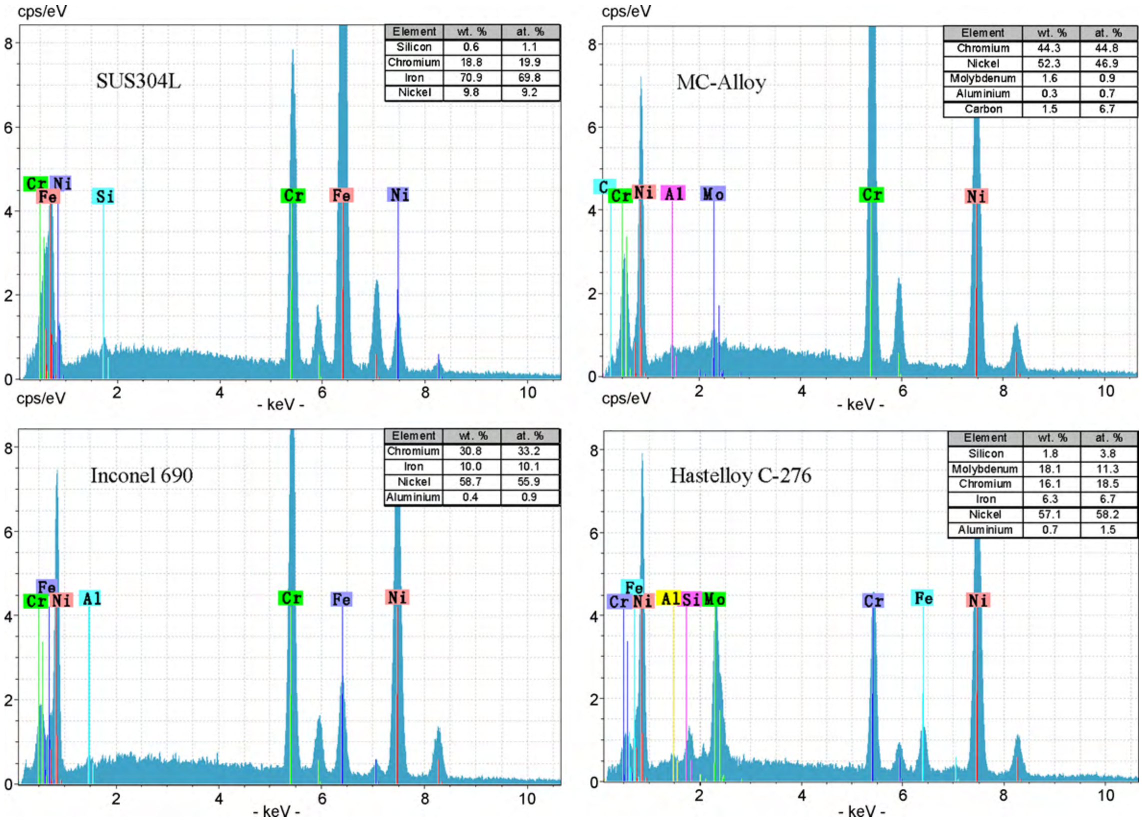


Fig. 8. EPMA results of commercial alloys.



SUS304L

Element	wt. %	at. %
Silicon	0.6	1.1
Chromium	18.8	19.9
Iron	70.9	69.8
Nickel	9.8	9.2

MC-Alloy

Element	wt. %	at. %
Chromium	44.3	44.8
Nickel	52.3	46.9
Molybdenum	1.6	0.9
Aluminium	0.3	0.7
Carbon	1.5	6.7

Inconel 690

Element	wt. %	at. %
Chromium	30.8	33.2
Iron	10.0	10.1
Nickel	58.7	55.9
Aluminium	0.4	0.9

Hastelloy C-276

Element	wt. %	at. %
Silicon	1.8	3.8
Molybdenum	18.1	11.3
Chromium	16.1	18.5
Iron	6.3	6.7
Nickel	57.1	58.2
Aluminium	0.7	1.5

Fig. 9. Effect of chromium content on corrosion rate.

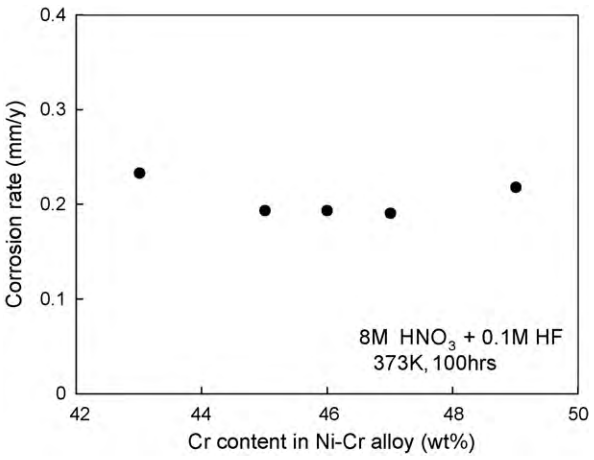


Fig. 10. Effect of chromium content in alloys on corrosion rate.

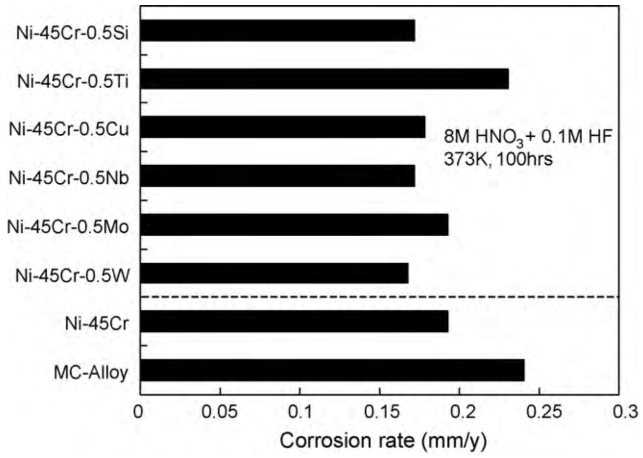


Fig. 11. Effect of third element addition on corrosion rate.

and the adding of the third element except molybdenum and titanium in Ni–45Cr alloy gave slight improvement of corrosion resistance. The error of corrosion rate between the same kinds of two samples was within ±4%, hence it is possible to compare with the corrosion rates between Ni–45Cr–0.5X alloys with reliability.

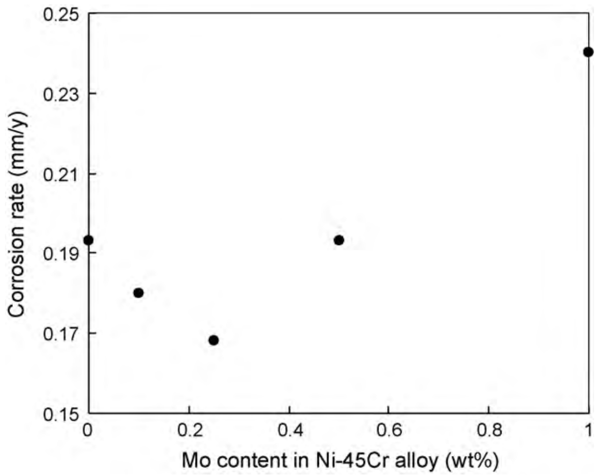


Fig. 13. Effect of molybdenum content in Ni–Cr alloys on corrosion resistance.

On the other hand, the adding of titanium in Ni–45Cr alloy gave the decrease of corrosion resistance. It is considered that the poor corrosion resistance of titanium in hydrofluoric acid influenced the corrosion rate of Ni–45Cr–0.5Ti alloy in HNO_3–HF mixtures. Fig. 12 shows the surface microstructures of Ni–45Cr–0.5X alloys after the corrosion test. There were no corrosion tracks on the all surfaces of Ni–45Cr–0.5X alloys. All of the corrosion rates of Ni–45Cr–0.5X alloys were less than 0.3 mm/y in 8 M HNO_3–0.1 M HF solutions at 373 K, and they were better than that of the MC alloy.

3.4. Effect of molybdenum content in Ni–45Cr alloys

The Ni–Cr–Mo alloy is known as one of the desirable corrosion resistant alloys in mixtures of oxidizing and reducing acids, in addition, a small amount addition of molybdenum contributes to accelerate the passive film formation on material surface [17]. From the results of the third step, the Ni–45Cr–0.5W alloy exhibited the best corrosion resistance. The molybdenum and tungsten are the same series elements, but the atomic mass of tungsten is nearly double of molybdenum. Accordingly, it can be supposed that the adding of 0.5 wt%W gives the same effect on the corrosion behavior as that of 0.25 wt%Mo. In the final step, the desirable molybdenum content in Ni–45Cr alloys for the improvement of cor-

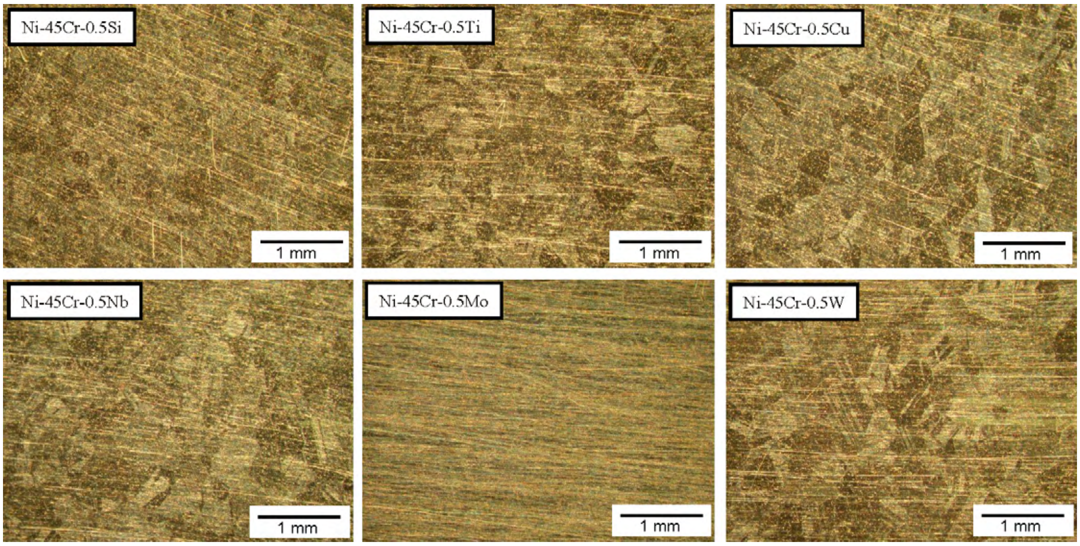


Fig. 12. Microstructure of Ni–45Cr–0.5X alloys after corrosion test.

rosion resistance was discussed in the small amount range of less than 1 wt%Mo. Fig. 13 shows the effect of molybdenum content in Ni–45Cr alloys on corrosion rate in 8 M HNO_3–0.1 M HF solutions at 373 K. Ni–45Cr–0.25Mo alloy exhibits the best corrosion resistance in the range of 0–1 wt%Mo. The corrosion rate was less than 0.17 mm/y and nearly equal to that of Ni–45Cr–0.5W alloy owing to the atomic mass effect. The desirable molybdenum or tungsten content in nickel-base alloy must depend on the ratio of hydrofluoric acid concentration to nitric acid concentration. In other words, the higher molybdenum content should be required to improve the corrosion resistance when hydrofluoric acid concentration becomes higher under constant nitric acid concentration condition. In conclusion, a small amount control of molybdenum is significant to improve the corrosion resistance of Ni–45Cr alloy in 8 M HNO_3–0.1 M HF solutions.

4. Conclusions

The effects of chromium and third element contents in nickel-base alloys were discussed to improve the corrosion resistance in hot HNO_3–HF mixtures. The chromium and molybdenum were greatly beneficial elements to improve the corrosion resistance in HNO_3–HF mixtures, and the delicate controls of 45 wt%Cr and 0.25 wt%Mo in nickel-base alloys exhibited the best corrosion resistance in 8 M HNO_3–0.1 M HF solutions. The corrosion rate was less than 0.17 mm/y and fully acceptable as equipment material. Thus, the nickel-base alloys controlled with higher chromium content and a small amount of molybdenum should be recommended as the alloy design to improve the corrosion resistance in hot nitric acid solution including a small amount of hydrofluoric acid.

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References

[1] O. Amano, K. Yasui, A. Sasahira, Y. Kani, M. Takahashi, T. Fukasawa, Y. Shibata, F. Kawamura, J. Nucl. Sci. Technol. (2002) 890–893 (Suppl. 3).
[2] Y. Kani, A. Sasahira, K. Hoshino, F. kawamura, J. Fluorine Chem. 130 (2009) 74–82.
[3] S. Ogata, S. Homma, A. Sasahira, F. Kawamura, J. Koga, S. Matsumoto, J. Nucl. Sci. Technol. 41 (2004) 135–141.
[4] R.D. Shaw, D. Elliott, Proc. Stainless Steels 84 (1984) 395–402.
[5] P. Fauvet, F. Balbaud, R. Robin, Q.-T. Tran, A. Mugnier, D. Espinoux, J. Nucl. Mater. 375 (2008) 52–64.
[6] A. Maki, JNC Tech. Rev. 14 (39–63) (2002) (in Japanese).
[7] F. Wada, Zairyo-to-Kankyo 48 (771–775) (1999) (in Japanese).
[8] D.F. Steele, Ind. Lubricat. Tribol. (Sep/Oct 1986) 164–169.
[9] B.F. Dunnett, G.O.H. Whillock, Corrosion 59 (3) (2003) 274–283.
[10] R. Robin, F. Miserque, V. Spagnol, J. Nucl. Mater. 375 (2008) 65–71.
[11] B.S. Covino, J.V. Scalera, T.J. Driscoll, J.P. Carter, Metallurg. Trans. A 17A (1986) 137–149.
[12] W.H. Smith, G.M. Purdy, Waste Manage. 15 (1995) 477–484.
[13] R. Mah, C.F. Braun, D.L. Cash, Mater. Perform. (1975) 28–31.
[14] E.-M. Horn, P.E. Manning, M. Renner, Werkstoffe Korrosion 43 (1992) 191–200.
[15] A.I. Asphahani, Arab. J. Sci. Eng. 14 (1989) 317–335.
[16] P. Crook, M.L. Caruso, D.A. Kingseed, J. Mater. Select. Des. (1997) 49–52.
[17] K. Sugahara, NACE Corrosion 2006, Paper No. 06532, San Diego, 2006.
[18] N. Sridhar, B.C. Wu, P.E. Manning, J. Met. (1985) 51–53.
[19] E.L.Hibner, NACE Corrosion/89, Paper No. 104, New Orleans, Louisiana, 1989.
[20] H.H. Uhlig, Corrosion and Control, John Wiley and Sons, 1963.
[21] W. Betteridge, J. Heslop, The Nimonic Alloy, Crank Russak and Company, 1974.
[22] R.B. Rebak, J.R. Dillman, P. Crook, C.V.V. Shawber, Mater. Corros. 52 (2001) 289–297.