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Corrosion Behavior of Amorphous Nickel-Valve Metal Alloys in Boiling Concentrated Nitric and Hydrochloric Acids*

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Synopsis

The corrosion behavior of amorphous nickel-base alloys containing titanium, zirconium, niobium, tantalum and/or phosphorus in boiling 9 N HNO_3 solutions with and without Cr^{6+} ion and in a boiling 6 N HCl solution was investigated. In boiling 9 N HNO_3 solutions alloys containing 20 at% or more tantalum were immune to corrosion, maintaining the metallic luster, and Ni-40∿60Nb alloys showed low corrosion rates of the order of μm/year. In the boiling 6 N HCl solution only tantalum-containing alloys were immune to corrosion although a higher tantalum content was required in the 6 N HCl solution in comparison with 9 N HNO_3 solutions. Protective surface films on the Ni-Nb and Ni-Ta-(P) alloys were composed exclusively of $NbO_2(OH)$ and $TaO_2(OH)$. Consequently, the corrosion resistance is not provided unless alloys contain elements, the passive film of which is highly stable in these aggressive boiling acids, such as tantalum.

I. Introduction

Commercial stainless steels have been known to suffer intergranular corrosion in hot concentrated nitric acids$^{1,2)}$. Among them low carbon austenitic stainless steels have a better corrosion resistance$^{3)}$. They have, however, still increasing tendency to intergranular corrosion when oxidizing species such as Cr^{6+} ion are further contained in these oxidizing acids. In this manner, alloys whose corrosion resistance relies on the presence of chromium cannot be used in such aggressive hot concentrated acids having a high oxidizing power.

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We have previously reported the corrosion behavior of amorphous nickel-valve metal alloys in boiling 9 N HNO_3 solutions with and without Cr^{6+} ion[4]. Although amorphous binary nickel-titanium and nickel-zirconium alloys were not sufficiently corrosion-resistant, amorphous alloys containing certain amounts of tantalum were almost immune to any forms of corrosion in these aggressive solutions due to formation of a passive tantalum oxyhydroxide film and were superior to crystalline tantalum metal. Accordingly, the oxidizing power of hot concentrated nitric aicds is too high to maintain the passivity of chromium but suitable for the passivity of tantalum.

On the other hand, hot concentrated hydrochloric acids are quite aggressive but have a poor oxidizing power, and hence corrode severely all conventional chromium-containing crystalline alloys. Nevertheless, some of amorphous Fe-Cr-Mo-P-C and Fe-Cr-Mo-C alloys are known to passivate spontaneously in hot concentrated hydrochloric acids[5,6]. However, the corrosion behavior of amorphous alloys in a boiling azotropic 6 N HCl solution is unknown. It is interesting to clarify the relationship between the passivating ability of amorphous alloys and the difference in oxidizing power of very aggressive boiling acids.

The present study has been performed to examine the corrosion resistance of various amorphous nickel-valve metal alloys in a boiling 6 N HCl solution in comparison with that in boiling 9 N HNO_3 solutions.

II. Experimental

Various nickel- and iron-base alloy casts were prepared by induction melting of commercial metals and home-made nickel phosphide, iron phosphide and iron carbide. Amorphous alloys were prepared in a ribbon shape by using the rotating wheel method. The formation of the amorphous structure was confirmed by X-ray diffraction. A commercial nickel-molybdenum alloy and home-made high purity stainless steel were used for comparison whose chemical compositions are shown in Table 1. Commercial crystalline titanium, zirconium, niobium and tantalum metals were also used for comparison.

Specimens which were polished mechanically with silicon carbide paper up to No.1000 in cyclohexane and rinsed ultrasonically with acetone were used for immersion tests and polarization measurements.

Table 1 Chemical compositions of commercial Ni-Mo alloy and home-made high purity stainless steel (wt%)

	Fe	Cr	Ni	Mo	Nb	C	Si	Co	Mn	P	S
Ni-Mo alloy	1.4	0.4	Bal	26.6	—	0.00	0.02	0.07	0.2	<0.005	0.00
Stainless steel	53.3	24.8	20.6	—	0.25	0.003	0.02	—	0.002	0.0002	—

After acetone-rinsed specimens were dried in a desiccator for 24 h, specimens were weighed by a microbalance. Immersion tests were conducted in boiling 9 N HNO_3 solutions with and without 100 ppm of Cr^{6+} ion and in a boiling 6 N HCl solution for 168 h. After rinsing with distilled water and drying in a desiccator for 24 h, the corrosion rate was estimated from the weight loss measured by the microbalance. The steady open circuit corrosion potential was attained by immersion for 40-50 min and then a potentiodynamic polarization curve was measured in these boiling solutions with a potential sweep rate of 100 mV/min.

Surface compositions after immersion tests were analyzed by using X-ray photoelectron spectra measured by Shimadzu ESCA 750 electron spectrometer with Mg Kα excitation.

III. Results

1. Immersion Tests

Boiling 9 N HNO_3

Figure 1 shows corrosion rates of amorphous nickel-titanium alloys as a function of concentration of various alloying elements. Corrosion rates of crystalline metals and stainless steel are shown for comparison in the left end of the figure, in which solid and open symbols correspond to data obtained in 9 N HNO_3 solutions with and without Cr^{6+} ion, respectively. Binary Ni-Ti alloys are corroded very rapidly, and increasing titanium content is not effective in decreasing the corrosion rate. Although it has been known that the corrosion resistance of amorphous Ni-Ti alloys in 1 N HCl and 1 N HNO_3 solutions at room temperature is remarkably improved by the addition of a small amount of phosphorus[7], the addition of phosphorus is not effective in improving the corrosion resistance in such aggressive acids having

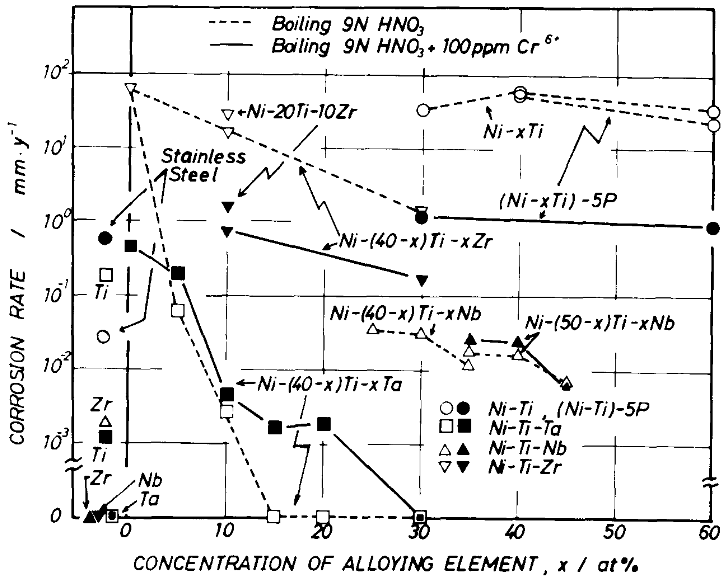

Fig. 1 Corrosion rates of amorphous Ni-Ti alloys in boiling 9 N HNO_3 solutions with and without Cr^{6+} ion.

a high oxidizing power. The substitution of zirconium, niobium or tantalum for titanium in Ni-Ti alloys results in a decrease in corrosion rate. Among them the substitution of tantalum is most effective. The alloy containing 30 at% tantalum shows undetectable corrosion weight loss even in the acid having a high oxidizing power by the Cr^{6+} ion addition. The alloy maintained its metallic luster after immersion tests in both solutions. Crystalline tantalum and niobium metals were also corrosion-resistant but lost their metallic luster by immersion tests. The corrosion resistance of titanium and zirconium is better in the solution with Cr^{6+} ion than in the solution without Cr^{6+} ion due to an enhancement of the protective quality of the surface film[8]. Similarly, the addition of Cr^{6+} ion to the solution results in an increase in corrosion resistance of amorphous Ni-Ti and Ni-Ti-Zr alloys. However, the Cr^{6+} ion addition to the solution is not effective for Ni-Ti-Nb alloys and is rather detrimental for Ni-Ti-Ta alloys.

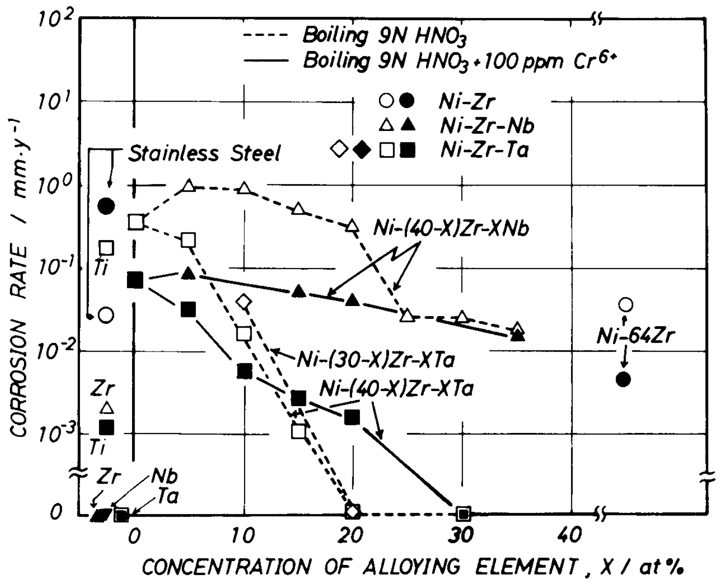

Fig. 2 Corrosion rates of amorphous Ni-Zr alloys in boiling 9 N HNO_3 solutions with and without 100 ppm Cr^{6+} ion.

Figure 2 shows corrosion rates of amorphous nickel-zirconium alloys. Corrosion rates of binary Ni-Zr alloys in boiling 9 N HNO_3 solutions are 2 to 3 orders of magnitude lower than those of binary Ni-Ti alloys, and the corrosion rates decrease by a factor of about 13 with increasing zirconium content from 40 to 64 at%. However, their corrosion rates are still higher than the crystalline zirconium metal. The substitution of niobium for zirconium in the Ni-40Zr alloy tends to decrease in corrosion rate. The substitution of tantalum for zirconium in Ni-Zr alloys is quite effective, and the Ni-10Zr-30Ta alloy shows the undetectable corrosion weight loss in both acids.

Figure 3 shows corrosion rates of amorphous nickel-niobium alloys. The corrosion resistance of amorphous binary Ni-Nb alloys is relatively better than that of Ni-Ti and Ni-Zr alloys, but is not sufficiently high. The surface became blue by immersion tests due to the formation of a thick corrosion product film. The addition of phosphorus to Ni-Nb alloys is rather slightly detrimental than beneficial in these acids having a high oxidizing power. The addition of tantalum is again quite effective, and the corrosion rate of Ni-Nb-Ta alloys becomes almost undetectable by the addition of 10 at% tantalum in the boiling 9 N HNO_3 solution and by the addition of 15 at% tantalum in the solution containing 100 ppm Cr^{6+} ion, although they became goldish.

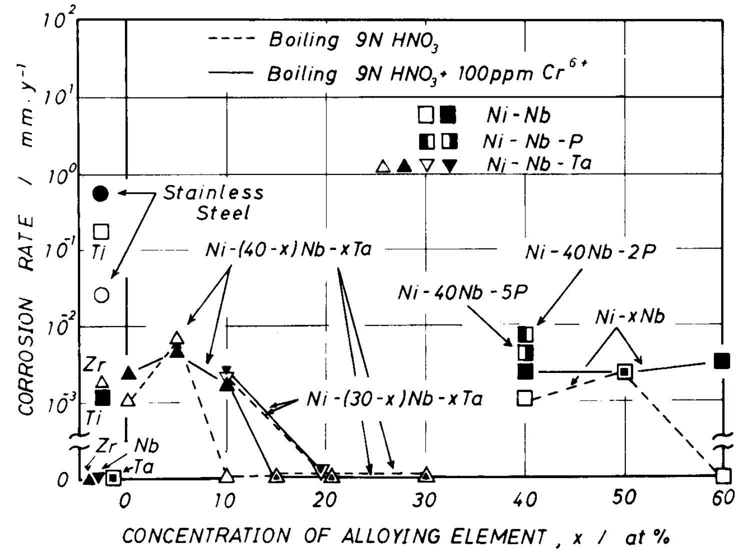

Fig. 3 Corrosion rates of amorphous Ni-Nb alloys in boiling 9 N HNO_3 solutions with and without 100 ppm Cr^{6+} ion.

Figure 4 shows corrosion rates of nickel-tantalum alloys. The binary alloy containing 10 at% tantalum was a mixture of amorphous and crystalline phases. The Ni-20Ta alloy consisted of a major amorphous phase and a minor crystalline phase. The Ni-10Ta alloy shows almost the same corrosion rate as that of the amorphous Ni-20Nb-10Ta alloy in the boiling 9 N HNO_3 solution, but is almost immune to corrosion in the boiling 9 N HNO_3 solution containing Cr^{6+} ion.

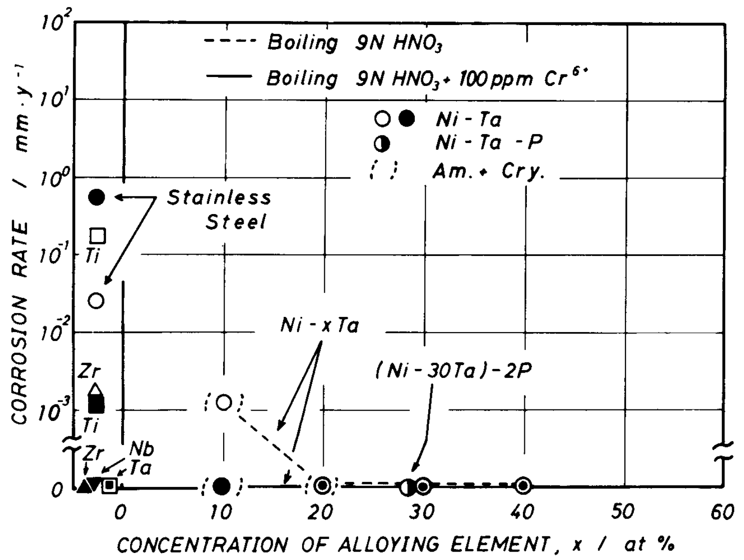

Fig. 4 Corrosion rates of amorphous Ni-Ta alloys in boiling 9 N HNO_3 solutions with and without 100 ppm Cr^{6+} ion.

Accordingly, nickel-valve metal alloys showed the corrosion resistance depending on the valve metal contained, and tantalum was the most effective alloying element, but titanium, zirconium and niobium contained in amorphous ternary Ni-

Ta-valve metal alloys were rather detrimental for the corrosion resistance provided by tantalum contained in these alloys in such aggressive acids having a high oxidizing power.

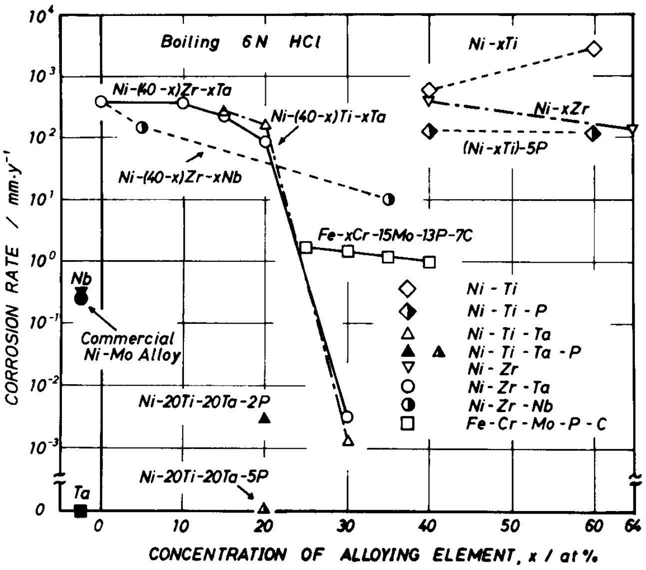

Fig. 5 Corrosion rates of amorphous Ni-Ti, Ni-Zr and Fe-Cr-Mo-13P-7C alloys in a boiling 6 N HCl solution.

Boiling 6 N HCl

Figure 5 shows corrosion rates of amorphous Ni-Ti, Ni-Zr and Fe-Cr-Mo-P-C alloys. Corrosion rates of commercial crystalline Ni-Mo alloy and niobium and tantalum metals are also shown for comparison. Binary Ni-Ti and Ni-Zr alloys suffer severe corrosion, and the addition of phosphorus to Ni-Ti alloys results only in a slight decrease in corrosion rate. The substitution of niobium for zirconium in the Ni-40Zr alloy decreases the corrosion rate. However, because the corrosion resistance of niobium metal itself is not sufficiently high, the effect of niobium addition is not significant. The substitution of tantalum for titanium or zirconium in Ni-40 Ti and Ni-40Zr alloys is not effective up to 20 at%, but corrosion rates of 30 at% tantalum alloys are in the order of μm/year. The addition of a small amount of phosphorus is particularly effective. The corrosion rate of amorphous Ni-20Ti-20Ta-2P alloy is about 3 μm/year, and the weight loss of the amorphous Ni-20Ti-20Ta-5P alloy was undetectable. On the other hand, it has

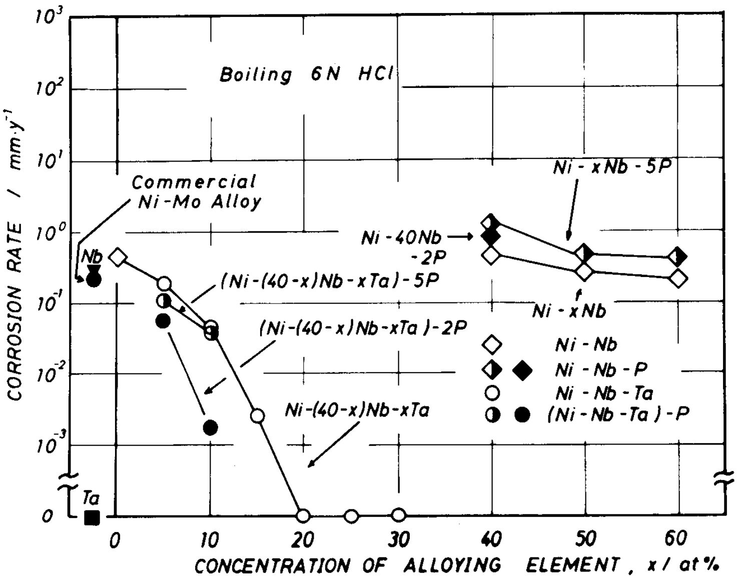

Fig. 6 Corrosion rates of amorphous Ni-Nb alloys in a boiling 6 N HCl solution.

been known that in a 6 N HCl solution at 80°C amorphous Fe-Cr-15Mo-13P-7C alloys containing 25 at% or more chromium passivate spontaneously, their corrosion rates being 0.1 mm/year or less. However, in the boiling 6 N HCl solution their corrosion rates are about one order of magnitude as high as those measured at 80°C.

Figure 6 shows corrosion rates of amorphous nickel-niobium alloys. Corrosion rates of binary alloys containing 40-60 at% niobium are about 3 orders of magnitude lower than those of amorphous Ni-Ti and Ni-Zr alloys, and are almost the same as the corrosion rate of the niobium metal, although their corrosion resistance is not sufficiently high. The substitution of tantalum for niobium in the binary alloys decreases the corrosion rate and the ternary Ni-Nb-Ta alloys containing 20 at% or more tantalum shows no corrosion weight losses. The addition of phosphorus to binary Ni-Nb alloys does not improve the corrosion resistance. However, the addition of 2 at% phosphorus to ternary Ni-30Nb-10Ta alloy decreases the corrosion rate by a factor of about 25, although the addition of 5 at% phosphorus to the same alloy is ineffective in decreasing the corrosion rate.

Figure 7 shows corrosion rates of nickel-tantalum alloys. Binary alloys containing 35 at% or more tantalum are immune to corrosion, maintaining a metallic luster. In contrast, crystalline niobium and tantalum metals suffer uneven general corrosion. The tantalum metal tinged with black after immersion and the niobium metal dissolved actively without forming an appreciable surface film. Ni-10Cr-30Ta, Ni-20Cr-20Ta and Ni-15Cr-25Ta alloys are all amorphous and their corrosion resistance is slightly better than that of binary Ni-Ta alloys containing similar amounts of tantalum. The addition of a small amount of phosphorus is remarkably effective. For instance, the corrosion rate of the amorphous Ni-10Ta-18P alloy is about one-eight hundredth as high as that of the Ni-10Ta alloy consisting of a mixture of amorphous and crystalline phases. The

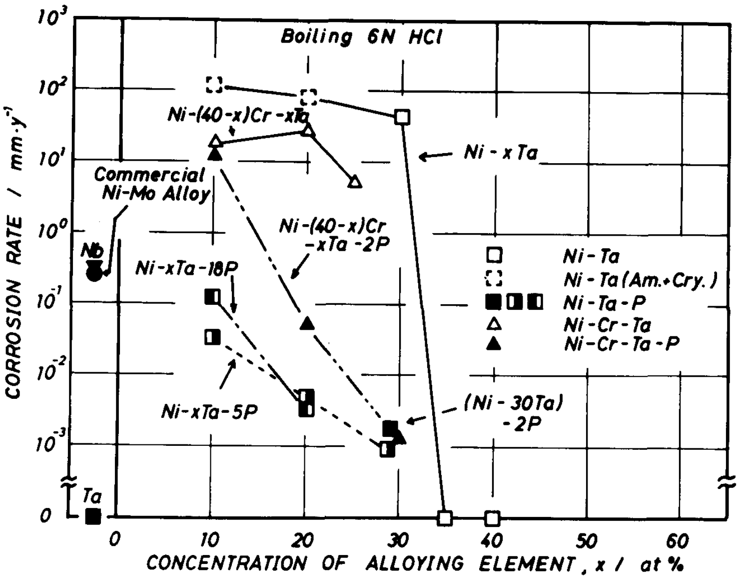

Fig. 7 Corrosion rates of amorphous Ni-Ta alloys in a boiling 6 N HCl solution.

corrosion rate of amorphous Ni-Cr-Ta alloys is also remarkably decreased by the addition of 2 at% phosphorus. The Ni-20Ta-5P alloy composed of a major amorphous phase and a minor crystalline phase shows almost the same corrosion rate as the amorphous Ni-20Ta-18P alloy.

Consequently, the addition of tantalum was quite effective in improving the corrosion resistance in both boiling hydrochloric and nitric acids. Furthermore, the phosphorus addition to alloys which was not effective in boiling nitric acids improved remarkably the corrosion resistance of tantalum-containing alloys in the boiling 6 N HCl solution but was not effective for other amorphous nickel-valve metal alloys without containing tantalum.

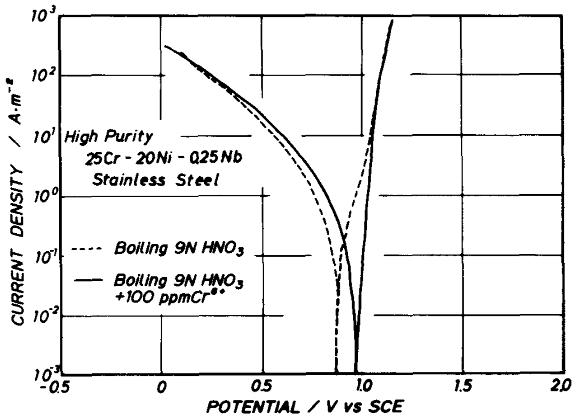

Fig. 8 Potentiodynamic polarization curves of home-made high purity stainless steel in boiling 9 N HNO_3 solutions with and without 100 ppm Cr^{6+} ion.

2. Polarization Curves

Boiling 9 N HNO_3

Because of the high oxidizing power of boiling 9 N HNO_3 solutions open circuit corrosion potentials of all the metals and alloys studied located in the potential range of 0.7-1.2 V vs. SCE. Their corrosion resistance seems, therefore, determined whether their passivity is stable in this potential range. As shown in Figure 8 the open circuit potential of the high purity austenitic stainless steel exceeds the stable passive range due to a violent cathodic reaction particularly in the solution containing Cr^{6+} ion. On the other hand, the crystalline tantalum metal is in the stable passive region as shown in Figure 9. Amorphous Ni-Ta alloys containing certain amounts of tantalum such as 30 at% or more were passive in boiling nitric acid solutions. Furthermore, as Figure 9 clearly illustrates,

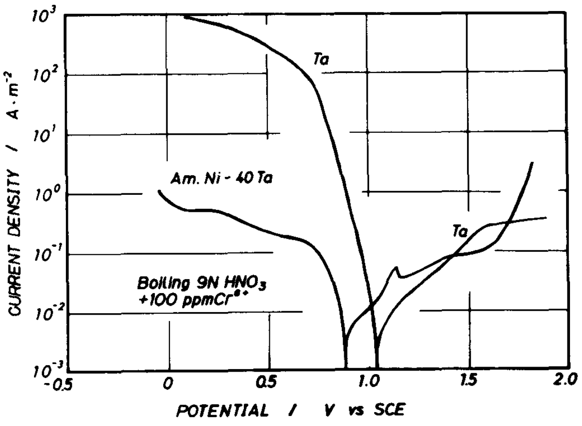

Fig. 9 Potentiodynamic polarization curves of crystalline tantalum metal and amorphous Ni-40Ta alloy in a boiling 9 N HNO_3 solution containing 100 ppm Cr^{6+} ion.

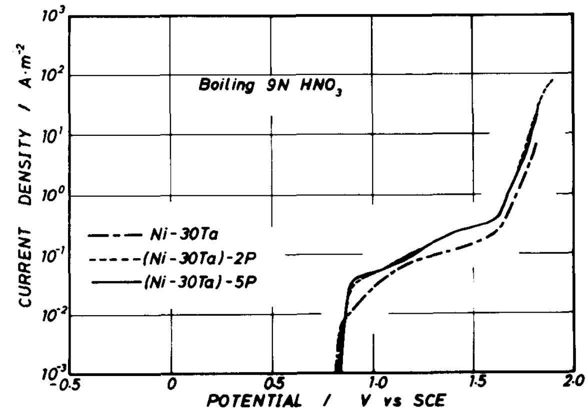

Fig. 10 Potentiodynamic polarization curves of amorphous Ni-30 Ta and (Ni-30Ta)-P alloys in a boiling 9 N HNO_3 solution.

these passive alloys are cathodically less active than the crystalline tantalum metal, indicating a better quality of the passive film on the tantalum-containing amorphous alloys in comparison with the crystalline tantalum metal. It has been known[7,9-11] that the phosphorus addition favors generally the passive film formation in acids of a low oxidizing power. However, since amorphous alloys containing certain amounts of tantalum produce a stable passive film in boiling nitric acids having a high oxidizing power, the addition of phosphorus does not appreciably change the polarization curve as shown in Figure 10 and was unnecessary and ineffective for the improvement of the passivity.

Boiling 6 N HCl

Because of a low oxidizing power only alloys having a high passivating ability are spontaneously passive in the boiling 6 N HCl solution. As shown in Figure 11 the amorphous Ni-30Ta alloy dissolves actively, but an increase in tantalum content decreases the anodic current density and ennobles the open circuit corrosion potential. The addition of 35 at% tantalum is required for spontaneous passivation of amorphous binary Ni-Ta alloys. This is in accord with the fact that the corrosion rate of Ni-30Ta alloy is about 44 mm/year, while the Ni-Ta alloys containing 35 at% or more tantalum are immune to corrosion. Accordingly, the corrosion resistance of various alloys in the boiling 6 N HCl solution is based on spontaneous passivation which is characterized by a large decrease in active dissolution current with a consequent ennoblement of the open circuit corrosion potential.

Figure 12 shows polarization curves of amorphous Ni-Nb

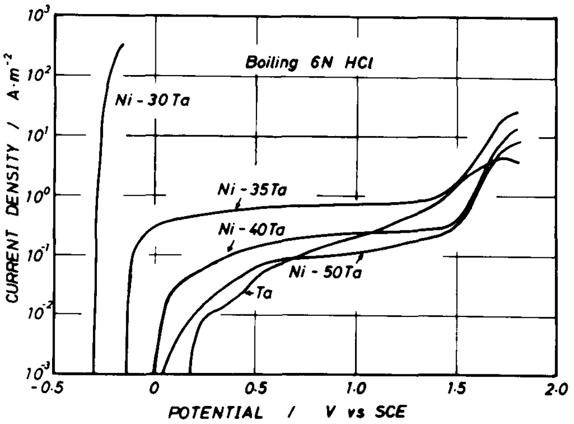

Fig. 11 Potentiodynamic polarization curves of amorphous Ni-Ta alloys in a boiling 6 N HCl solution.

alloys and crystalline niobium metal. The open circuit corrosion potential of amorphous alloys is 140 mV or more as high as that of the crystalline niobium metal. Since corrosion rates of amorphous Ni-Nb alloys are not largely different from the corrosion rate of crystalline niobium metal as shown in Figure 6, the higher open circuit potential is attributable to higher cathodic activities of alloys due to alloying with nickel and vitrification. On the other hand, an increase in niobium content of binary amorphous Ni-Nb alloys from 40 to 60 at% results in no ennoblement of open circuit corrosion potential. This suggests no significant decrease in anodic dissolution current with an increase in niobium content around the open circuit potential, being in agreement with no significant decrease in corrosion rate with increasing niobium content. A decrease in current density with the increase in niobium content in the potential region where surface films are stable is observed, suggesting an enhancement of protective quality of the surface film.

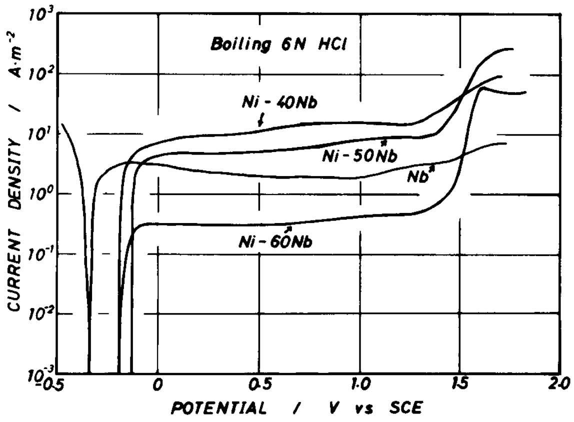

Fig. 12 Potentiodynamic polarization curves of amorphous Ni-Nb alloys in a boiling 6 N HCl solution.

As shown in Figure 13 the addition of phosphorus enhances significantly the passivating ability of Ni-Ta alloys. Not only the (Ni-30 Ta)-5P alloy but also Ni-20Ta-5P and Ni-20Ta-18P alloys passivate spontaneously as a result of decreasing current for active dissolution, whereas the Ni-30Ta alloy dissolves actively. This illustrates a large difference in corrosion rates between the Ni-30Ta alloy and various phosphorus-containing Ni-Ta alloys as shown in Figure 7.

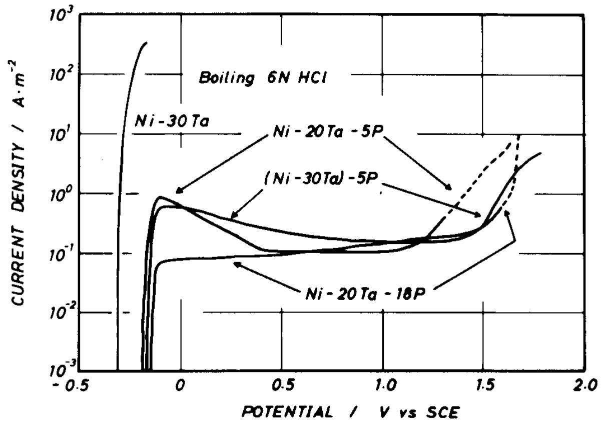

Fig. 13 Potentiodynamic polarization curves of amorphous Ni-30 Ta and Ni-Ta-P alloys in a boiling 6 N HCl solution.

As shown in Figure 14 the amorphous Ni-10Cr-30Ta alloy passivates spontaneously, while the amorphous Ni-20Cr-20Ta alloy dissolves actively. The fact that the addition of 10 at% chromium to Ni-30Ta alloy led to spontaneous passivation reveals the beneficial effect of chromium in increasing the passivating ability in the boiling 6 N HCl solution, although the passivity based on the presence of only chromium is less stable than the passivity due to a combined addition of tantalum and chromium as can be seen in Figures 5 and 7. Phosphorus is again quite effective alloying element in improving the passivating ability since the addition of 2 at% phosphorus to the Ni-20Cr-20Ta alloy leads to spontaneous passivation.

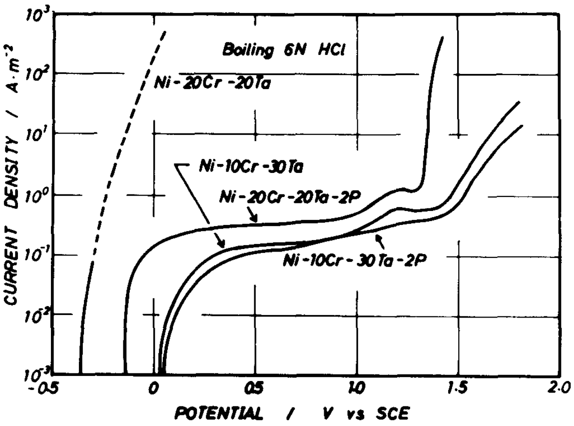

Fig. 14 Potentiodynamic polarization curves of amorphous Ni-Cr-Ta and Ni-Cr-Ta-P alloys in a boiling 6 N HCl solution.

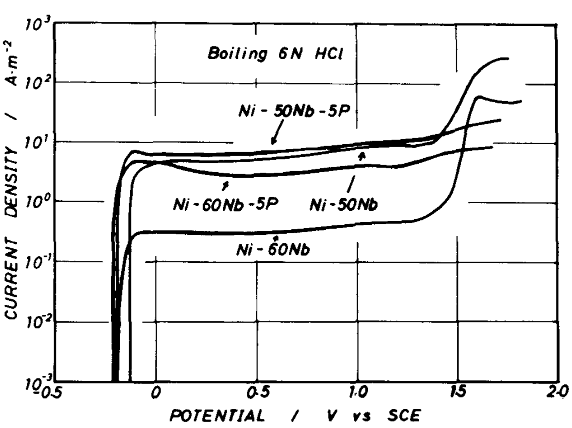

Fig. 15 Potentiodynamic polarization curves of amorphous Ni-Nb and Ni-Nb-5P alloys in a boiling 6 N HCl solution.

Figure 15 reveals no beneficial effect of phosphorus addition on the passivating ability of amorphous Ni-Nb alloys. This seems due to the fact that niobium metal itself has a relatively low passivating abililty in such an aggressive boiling hydrochloric acid, and shows a relatively high anodic current density in the passive region as shown in Figure 12.

3. Surface Analysis

X-ray photoelectron spectroscopy was applied to analyze the surfaces of amorphous Ni-40Nb, Ni-30Ta, Ni-35Ta and (Ni-30Ta)-2P alloys immersed for 1 h in boiling 9 N HNO_3 and 6 N HCl solutions. All specimens immersed in the boiling 9 N HNO_3 solution showed no detectable signals of the metallic state in Ni $2p_{3/2}$, Nb 3d and Ta 4f spectra due to the formation of surface films thicker than about 10 nm.

The Ni-35Ta alloy whose corrosion weight loss in the boiling 6 N HCl solution was undetectable exhibited clearly the Ta 4f spectrum from the metallic state along with the Ni $2p_{3/2}$ spectrum from the metallic state. Other specimens immersed in the boiling 6 N HCl solution showed a weak metallic signal of the Ni $2p_{3/2}$ spectrum but no metallic signal of the Ta 4f spectrum. Accordingly, the thinnest passive film was formed on the corrosion-resistant Ni-35Ta alloy by spontaneous passivation in the boiling 6 N HCl solution. Surface films formed on other alloys in the boiling 6 N HCl solution were thinner than surface films formed in the boiling 9 N HNO_3 solution, although the films formed in the boiling 6 N HCl solution were thicker than the passive chromium oxyhydroxide film of 1-4 nm thickness formed on chromium-containing alloys[6,9,11-14).

Nickel ion was scarcely contained in surface films because the Ni $2p_{3/2}$ spectrum from the oxidized state was hardly detected. Concentrations of phosphate, nitrate and chloride ions in surface films were extremely low since P 2p, N 1s and Cl 2p spectra were hardly detected. The Ta $4f_{7/2}$ spectrum showed the peak binding energy at about 26.1 eV, and the Nb $3d_{5/2}$ spectrum exhibited the peak at about 207.5 eV. They were assumed to be in the pentavalent state. The O 1s spectrum indicated that the surface film was composed of two kinds of oxygen species, that is, O^{2-} and OH^- 15). The OH^- comprised about one-third of oxygen species. After quantitative determination13,16) the surface films were identified as single films of $NbO_2(OH)$ on the Ni-40 Nb alloy and $TaO_2(OH)$ on the tantalum-containing alloys regardless of the presence or absence of phosphorus in alloys.

IV. Discussion

The X-ray photoelectron spectroscopic examination revealed that passive films formed on amorphous Ni-Ta and Ni-Nb alloys in boiling 9 N HNO_3 and 6 N HCl solutions are composed exclusively of $TaO_2(OH)$ and $NbO_2(OH)$, respectively. Because nickel is not corrosion-resistant in these boiling acids, the corrosion resistance of amorphous nickel-valve metal alloys depends upon the protective quality of the passive film consisting of valve metal ions as cations. Passive films composed of titanium or zirconium ions are not highly protective in these very aggressive boiling acids. Niobium-containing alloys were colored in boiling 9 N HNO_3 solutions, and their corrosion rates were in the order of μm/year, whereas they dissolved at the rate of several hundred μm/year in the boiling 6 N HCl solution. Accordingly, the passive film formed on the niobium-containing alloys, that is, the passive $NbO_2(OH)$ film seems not highly protective in the boiling 6 N HCl solution.

Nickel alloys containing certain amounts of tantalum were spontaneously passive in these acids and showed undetectable corrosion weight loss. The corrosion weight loss of binary Ni-Ta alloys became undetectable at 20 at% tantalum in boiling 9 N HNO_3 solutions. In the boiling 6 N HCl solution, Ni-35Ta, Ni-20Nb-20Ta and Ni-20Ti-20Ta-5P alloys showed undetectable corrosion weight losses, and ternary Ni-20∿30 Ta alloys containing phosphorus exhibited a very low corrosion weight loss. Consequently, the passive $TaO_2(OH)$ film seems very stable in these aggressive acids.

The addition of phosphorus to tantalum-containing alloys was quite effective in improving the corrosion resistance and passivating ability in the boiling 6 N HCl solution. Since the phosphate content of the passive film formed on Ni-Ta-P alloys was very low, phosphorus appeared to enhance the formation of the passive $TaO_2(OH)$ film without constituting the passive film. The passive film, in which beneficial ions are concentrated, is formed as a result of selective dissolution of alloy constituents unnecessary for the passive film formation14). Phosphorus, which is not the constituent of the passive film having the high protective quality, favors generally the active dissolution of alloy constituents unnecessary for passive film formation, and hence accelerates the formation of the passive film in which the beneficial ions are extraordinarily concentrated11,14). The boiling 6 N HCl solution is very aggressive and poorly oxidizing, in which accumulation of beneficial tantalum and hydroxyl ions at the interface between the solution and the Ni-30Ta alloy is difficult due to rapid active dissolution of all alloy constituents. Under such a condition, the addition of phosphorus to the alloy accelerates selective dissolution of alloy constituents unnecessary for the passive film formation, and hence is quite effective for the formation of the passive film consisting exclusively of tantalum oxyhydroxide.

On the other hand, boiling 9 N HNO_3 solutions are also very aggressive and have a very high oxidizing power. Accordingly, the passive tantalum oxyhydroxide and niobium oxyhydroxide films were easily formed in the boiling 9 N HNO_3 solutions on Ni-Ta and Ni-Nb alloys, and hence the phosphorus addition was not necessary and ineffective for the formation of passive films in which tantalum or niobium ions are highly concentrated.

It has been known7) that the phosphorus addition to Ni-Ti alloys significantly enhances the passivating ability and corrosion resistance in 1 N HCl and 1 N HNO_3 solutions at room temperature. However, an increase in corrosion resistance by the phosphorus addition to amorphous Ni-Ti and Ni-Zr alloys was not found in boiling 9 N HNO_3 solutions, and was very small in the boiling 6 N HCl solution. The fact that phosphorus is a very minor constituent of highly protective passive films formed on phosphorus-containing amorphous alloys, to which the phosphorus addition is quite effective, has been well known for passive hydrated chromium oxyhydroxide film[6,11,12)] and is reconfirmed in the present study for the passive tantalum oxyhydroxide film. It can, therefore, be said that the beneficial effect of the phosphorus addition in enhancing the passivating ability and corrosion resistance appears only when the passive film formed is very stable in the environment under consideration. Since passive titanium and zirconium oxyhydroxide films are not sufficiently stable and protective in these concentrated boiling acids, the enhancement of the passive film formation based on the phosphorus addition to Ni-Ti and Ni-Zr alloys is ineffective in improving the passivating ability and corrosion resistance. Similarly, the passive niobium oxyhydroxide film itself is not sufficiently stable in the boiling 6 N HCl solution, and hence the enhancement of passivation by the phosphorus addition to Ni-Nb alloys is ineffective.

V. Conclusions

The corrosion behavior of amorphous nickel-valve metal alloys in boiling 9 N HNO_3 solutions with and without Cr^{6+} ion and in a boiling 6 N HCl solution was investigated with a view to obtaining extremely corrosion-resistant alloys capable of maintaining the metallic luster without showing the corrosion weight loss higher than μm/year.

In boiling 9 N HNO_3 solutions Ni-Ta alloys containing 20 at% or more tantalum were immune to corrosion, and Ni-40∿60Nb alloys exhibited the corrosion rate of the order of μm/year. Other alloys were more or less corroded in these solutions. The immunity to corrosion in the boiling 6 N HCl solution required the addition of much higher concentration of tantalum such as 35 at% or a combined addition of tantalum and niobium or tantalum and phosphorus.

The ternary Ni-20∿30Ta-P alloys exhibited very low corrosion weight losses. The phosphorus addition to the tantalum-containing alloys was remarkably effective in enhancing the corrosion resistance in the boiling 6 N HCl solution, but was ineffective in the boiling 9 N HNO_3 solutions.

The high corrosion resistance of tantalum-containing alloys was due to the formation of a passive $TaO_2(OH)$ film. Other oxyhydroxide films consisting of titanium, zirconium or niobium ions appear less stable in these aggressive acids. Phosphorus contained in alloys did not constitute the protective tantalum oxyhydroxide film.

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