Corrosion Behavior of Tentative Nickel Binary and Ternary Alloys after Plasma Ion Nitriding Treatment†

—Studies on Surface Modification of Non Ferrous Metals by means of Plasma Ion Nitriding (PIN) Process (Report 3)—

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Abstract

In order to investigate the corrosion properties of Ni alloys after nitriding treatment, tentative Ni binary alloys of Ni-7wt%Ti, -15wt%V, -10wt%Nb, -20wt%Cr and -30wt%Cr and Ni ternary alloys of Ni-7wt%Ti-2wt% (V, Nb, Ta, Cr, Mo or Al) and Ni-20wt%Cr-2wt%(Ti, V, Nb, Ta, Mo or Al) were nitrided by means of plasma ion nitriding (PIN) process under the conditions of 873K (823K at Ni-30wt%Cr), 10.8ks, N_2+H_2 mixed gas atmosphere of 800Pa. Corrosion properties of tentative Ni alloys were determined by means of potentiodynamic polarization methode in an acid solution (30°C, 5%H_2SO_4). Pure nickel and austenitic stainless steel, SUS304 were also used as reference materials.

Tentative Ni alloys showed better corrosion resistance than pure nickel before PIN treatment. PIN treatment resulted in a slight deterioration of corrosion resistance of tentative Ni alloys. Comparing of corrosion resistance of Ni alloys with SUS 304 after PIN treatment, deterioration of corrosion resistalnce of Ni alloys were slighter than SUS304. Spalling of nitrided layer occurred in nitrided Ni-Cr binary alloys. On the contrary, Pitting and intergranular corrosion were observed in nitrided Ni binary and ternary alloys except Ni-Cr alloys.

Taking into consideration of corrosion resistance and hardenability by PIN treatment, Ni-7wt%Ti binary alloy, Ni-7wt%Ti-X and Ni-20wt%Cr-X ternary alloys were proved to be beneficial alloys as hardenable Ni alloys by PIN treatment.

KEY WORDS: (Plasma Nitriding) (Ion Nitriding) (Nitriding) (Nickel Alloy) (Corrosion Resistance) (Anodic Polarization)

1. Introduction

In the previous paper[1-3], the feasibility of the surface hardening of nickel (Ni) alloys by means of plasma ion nitriding (PIN) process was investigated for various commercially used Ni alloys and tentative Ni binary and ternary alloys containing nitride forming elements of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Al, or Si. As the results, it was made clear that Ti, V, Nb and Cr were the most benefitial alloying elements for surface hardning of Ni alloys by PIN treatment[1,2]. Moreover, the improvement of wear resistant of these alloys were observed after PIN treatment[3]

On the other hand, it is well known that the corrosion resistance of stainless steels were markedly deteriorated by nitriding treatment due to the Cr depleted zone caused by the precipitation of Cr nitride in nitrided layer[4].

On the contrary, corrosion resistance of nickel is much higher than iron. Therefore, at nitriding treatment of Ni-Cr alloys, it is presumed that a deterioration of corrosion resistance of nitrided Ni-Cr alloys is much slighter than ferrous alloys in spite of Cr depletion in Ni alloy matrix owing to the precipitate of Cr nitride by nitriding treatment.

However, there are no report with respect to corrosion behaivor of Ni alloys after PIN treatment, because there were few study of PIN treatment of Ni alloys so far.

Therefore the aim of this paper is to characterize the fundamental corrosion behavior of nitrided layers of Ni alloys containing nitride forming elements after PIN treatment. Corrosion resistance of Ni alloys after PIN treatment were evaluated by potentiodynamic polarization methode.

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2. Experimental Procedure

2.1 Materials used

Five kinds of tentative Ni binary alloys and twelve kinds of tentative Ni ternary alloys which showed remarkable surface hardening by PIN treatment[1-3] were used in this investigation. These tentative Ni alloys were prepared with high frequency induction melting in argon atmosphere. These alloys were rolled at 1273K after casting and then annealed at 1073K for 10.8Ks. Chemical compositions of these alloys were shown in **Table 1**. Pure Ni and 18Cr-8Ni austenitic stainless steel type SUS304 were also used for comparison. Specimen size for PIN treatment was 10mm in width, 20mm in length and 3mm in thickness. A specimen surface was polished by emery paper up to grade 1200 and degreased with acetone before PIN treatment.

Table 1 Chemical composition of tentative Ni binary and ternary alloys

Alloy	X	Chemical composition (wt%)							
		Ti	V	Nb	Ta	Cr	Mo	Al	Ni
Ni-7Ti	–	7.19	–	–	–	–	–	–	bal.
Ni-15V	–	–	14.87	–	–	–	–	–	bal.
Ni-10Nb	–	–	–	9.97	–	–	–	–	bal.
Ni-20Cr	–	–	–	–	–	20.54	–	–	bal.
Ni-30Cr	–	–	–	–	–	29.15	–	–	bal.
Ni-7Ti-X	2V	7.33	2.02	–	–	–	–	–	bal.
	2Nb	7.08	–	2.04	–	–	–	–	bal.
	2Ta	7.69	–	–	1.92	–	–	–	bal.
	2Cr	6.99	–	–	–	1.94	–	–	bal.
	2Mo	7.19	–	–	–	–	1.95	–	bal.
	3Al	6.94	–	–	–	–	–	2.72	bal.
Ni-20Cr- X	2Ti	2.00	–	–	–	19.05	–	–	bal.
	2V	–	1.94	–	–	19.75	–	–	bal.
	2Nb	–	–	1.68	–	19.50	–	–	bal.
	2Ta	–	–	–	2.09	21.59	–	–	bal.
	2Mo	–	–	–	–	20.51	1.99	–	bal.
	2Al	–	–	–	–	20.40	–	1.64	bal.

2.2 Plasma ion nitriding process and corrosion test

Plasma ion nitriding apparatus was the same as that in the previous work[1]. PIN condition was kept constant at the adequate values as follows; nitriding gas was a mixed gas of nitrogen and hydrogen (nominal purity 99.9999%, 50vol%N_2+50vol%H_2) and its gas pressure was 800Pa. Nitriding temperature was 823K for Ni-30Cr and 873K for all the other alloys. At these nitriding temperature, surface hardness of specimen after PIN treatment showed its maximum value for each alloy. Corossion resistance of untreated and nitrided specimens were determined by anodic polarization curve measured by potentiodynamic polarization methode in deaerated 5%H_2SO_4 solution at 303K and scan rate of 20mV/min. Potential was measured against a platinum electrode, and it was expressed relative to the saturated calomel electrode (SCE). After measurement of anodic polarization curve, polarization potential and current density of nitrided alloys were compared with untreated one. Moreover, surface sppearance and microstructure of nitrided layer after anodic polarization measurement were observed by optical microscope.

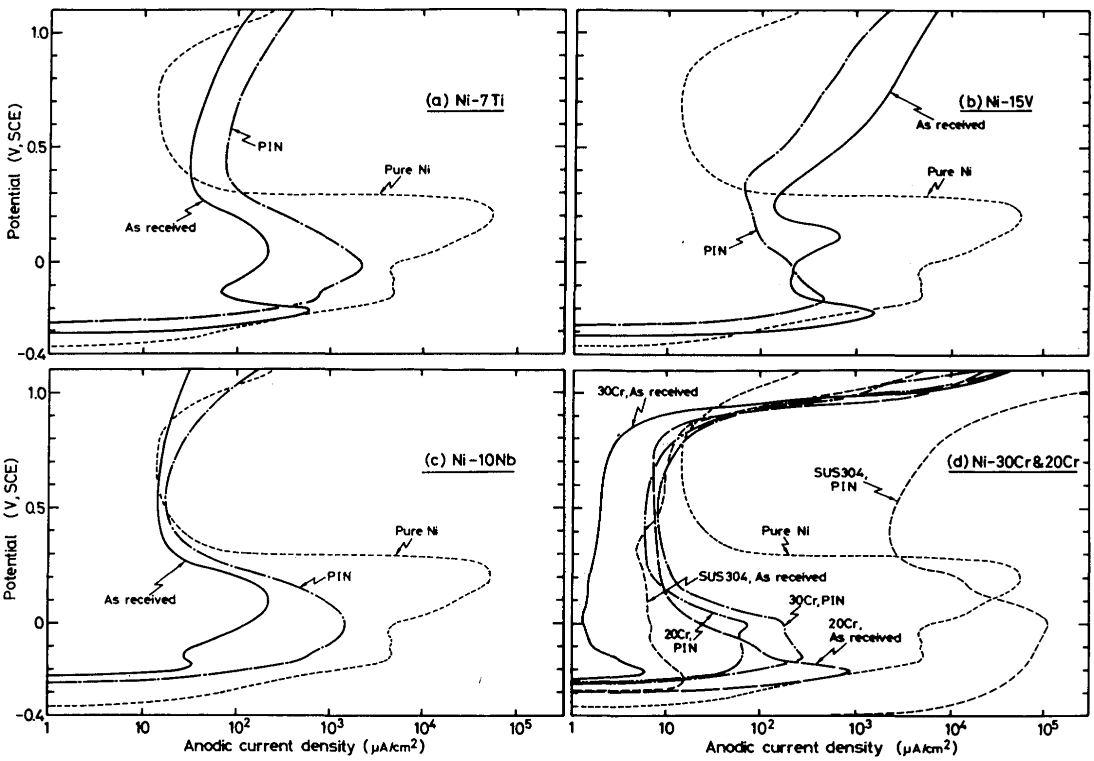

Fig. 1 Anodic polarization curve for Ni binary alloys, pure Ni and 18Cr-8Ni (SUS304)

3. Results and discussions

3.1 Anodic polarization properties after PIN treatment

As a preliminary investigation, anodic polarization curve of untreated and nitrided Ni binary allloys has been investigated by using potentiodynamic polarization methode. Moreover, pure Ni and 18Cr-8Ni steel were also used for comparison.

Figure 1 (a) to **(d)** shows the polarization curve of both untreated and nitrided Ni binary alloys of Ni-7Ti, 15V, 10Nb, 30Cr and 20Cr. Dashed lines in Fig. 1 indicate polarization curve of pure Ni and 18Cr-8Ni steel.

Pure Ni showed typical polarization curve indicating active, passive and transpassive regions.
The polarization curve of tentative Ni binary alloys were affected by the kind of alloying element and PIN treatment. Polarization current density of nitrided Ni-7Ti was higher than untreated one. Both untreated and nitrided specimens showed lower current density than pure Ni in active region, though current density in passive region was higher than pure Ni. Untreated Ni-15V showed lower current density than pure Ni in active region, but in passive region it was higher than pure Ni. However, current density of nitrided Ni-15V became lower than untreated one in each region. Current desity of Ni-10Nb was increased by PIN treatment, but its current density was same or lower than pure Ni.

In Ni-30Cr and 20Cr binary alloys, current density of untreated Ni-30Cr was the lowest of all tentative Ni alloys, but it was also increased by PIN treatment. The properties of anodic polarization current density of untreated and nitrided Ni-20Cr were similar to Ni-30Cr.

Anodic polarization properties of 18Cr-8Ni steel were compared with these Ni binary alloys. Polarization current density of untreated 18Cr-8Ni steel in active region was similar to Ni-20Cr and current density in passive region was slightly higher than Ni-20Cr. However, the current density of 18Cr-8Ni steel was remarkably increased by PIN treatment and was higher than pure Ni. Therefore, corrosion resistance of 18Cr-8Ni steel was markedly deteriorated by nitriding treatment as well known. On the contrary, the increase in current density of tentative Ni alloys by PIN treatment were much lower than 18Cr-8Ni steel.

Generally, critical passivation current density, i_{crit}, and minimum current density in passive region, i_{min}, on the anodic polarization curve are used for the criteria of corrosion resistance. **Figure 2** shows the comparison of these values of i_{crit} and i_{min} measured from the polarization curve in Fig. 1 for untreated and nitrided Ni binary alloys, pure Ni and 18Cr-8Ni steel. All these values of tentative Ni alloys excepting Ni-15V alloy were increased by PIN treatment. However, the increase of these values of Ni

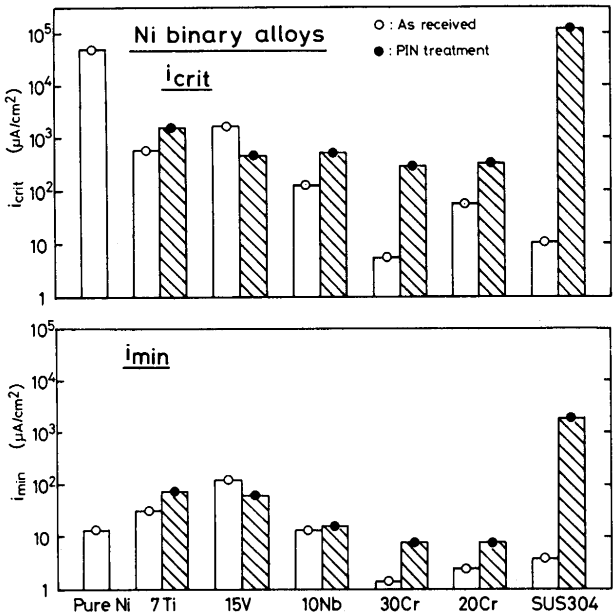

Fig. 2 Comparison of i_{crit} and I_{min} in anodic polarization curve of Ni binary alloys before and after PIN treatment

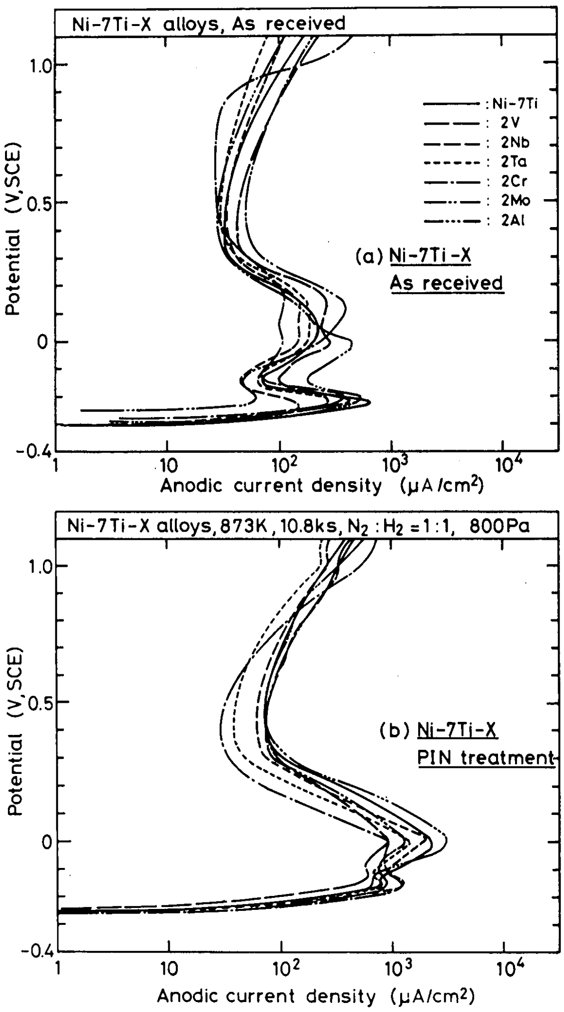

Fig. 3 Anodic polarization curve for Ni-7Ti-X alloys

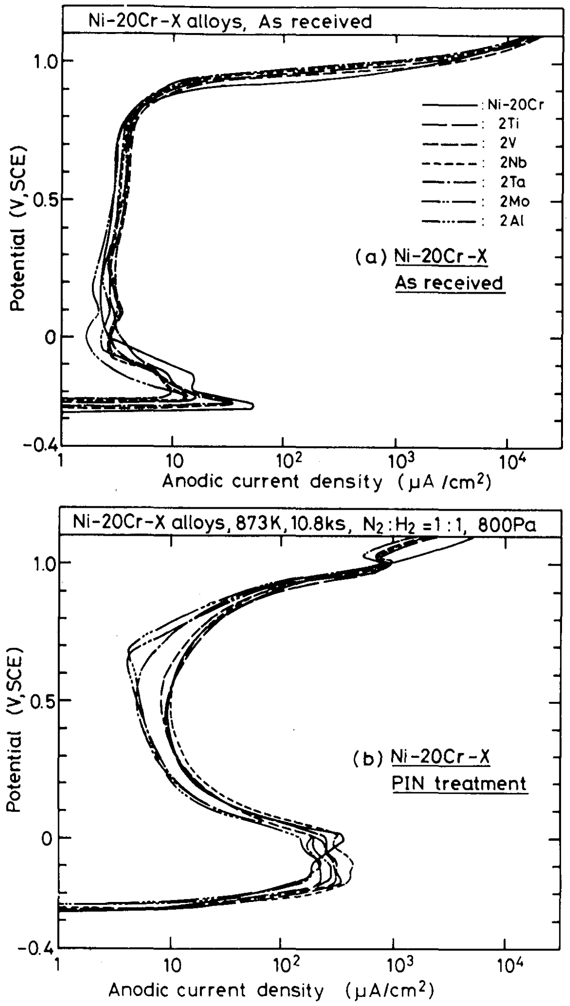

Fig. 4 Anodic polarization curve for Ni-20Cr-X alloys

alloys by PIN treatment were much smaller than nitrided 18Cr-8Ni steel. Ni-15V showed the decrease in these values by PIN treatment.

Moreover, in comparison with tentative Ni binary alloys and pure Ni, these values of tentative Ni binary alloys were lower than pure Ni. The slightly higher values of i_{min} of PIN treated Ni-7Ti and 15V were due to their high values in untreated condition. This means that corrosion resistance of these tentative Ni binary alloys after PIN treatment were higher than pure Ni. Therefore, it is considered that tentative Ni binary alloys possess comparably good corrosion resistance even after PIN treatment. However, the reason for the bahavior of anodic polarization curve of Ni-15V after PIN treatment has not been made clear in this paper.

Nextly, **Figures 3** and **4** show the anodic polarization curve of both untreated and nitrided tentative Ni ternary alloys of Ni-7Ti-X and Ni-20Cr-X, respectively. The effect of PIN treatment on the anodic polarization properties of these ternary alloys were almost the same to those of Ni binary alloys in each alloy system.

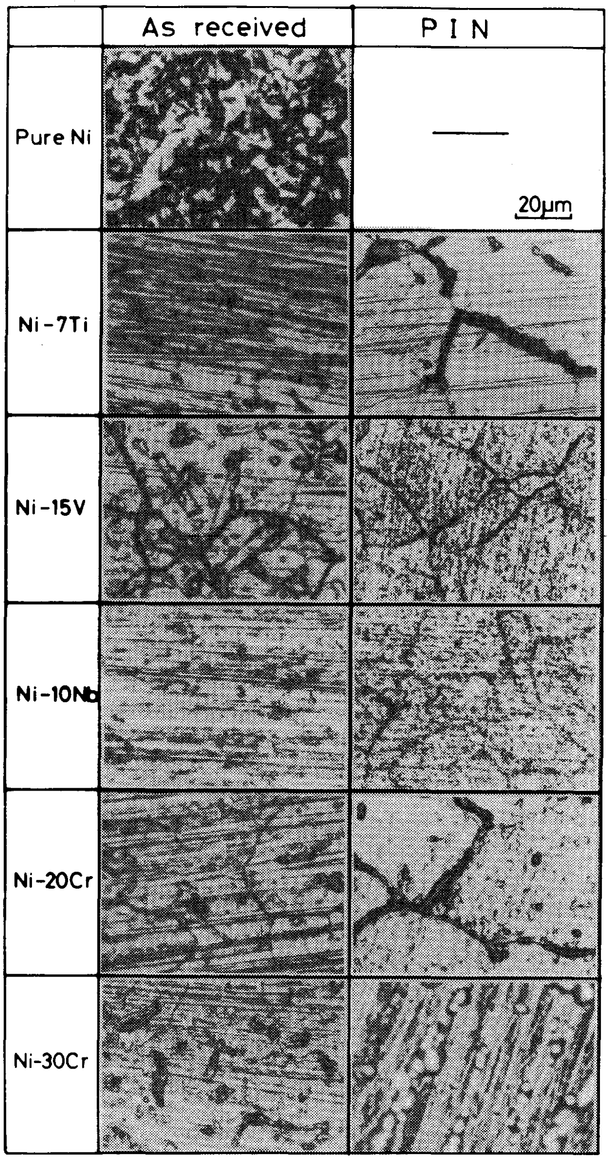

Fig. 5 Surface appearance of tentative Ni binary alloys after anodic polarization analysis

3.2 Surface appearance and microstructure of nitrided layer

Figure 5 shows the typical surface appearance of untreated and nitrided tentative Ni binary alloys and pure Ni after measurement of polarization curve. Surface of pure Ni was very rough, because corrosion resistance of pure Ni was more inferior than Ni binary alloys.

On the contrary, corrosion appearance of Ni binary alloys were much different depending on the kind of alloying element. In the untreated alloys, the surface of Ni-7Ti and 15V showed the uniform corrosion morphology, but the other Ni binary alloys showed the localized corrosion such as pittinng and intergranular corrosion.

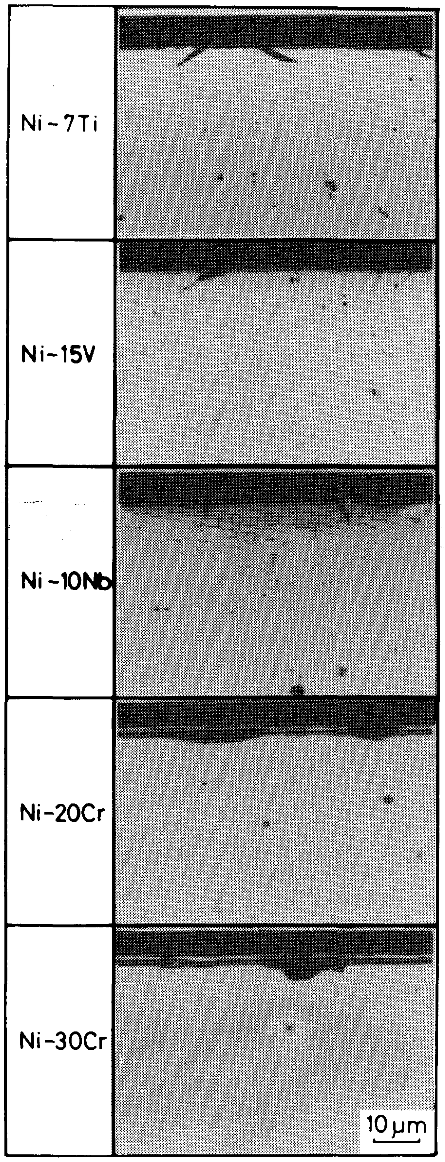

Fig. 6 Microstructure on crosssection of nitrided Ni binary alloys after anodic polarization analysis

Moreover, in the PIN treated alloys, the localized corrosion such as pitting and intergranular corrosion were observed in all Ni binary alloys. Therefore, it is considered that anodic polarization current density shown in Fig. 1 were the composited current density comprised the localized and the uniform corrosions.

Figure 6 shows the typical crosssectional microstructures of nitrided layer by electrolitically etched with 10% oxialic acid solution after the measurement of anodic polarization curve. Excepting Ni-Cr binary alloys, Ni binary alloys showed only the localized corrosion along grain boundary in nitrided layer.

On the contrary, in Ni-Cr binary alloys, the nitrided layer of these alloys was composed of double layer, and the inner layer was markedly corroded and corrosion cavity was preferentially formed in the inner layer just below the outer layer where localized corrosion was occurred due to the pitting and intergranular corrosion. Therefore, corrosion resistance of the outer nitridrd layer of Ni-Cr binary alloys is superior to the inner layer. However, it is considered that corrosion cavity formation in inner layer will cause the spalling of the outer nitrided layer.

Nextly, **Figures 7** and **8** show typical surface appearance and crosssectional microstructure of nitrided Ni ternary alloys after anodic polarization curve measurement, respectively. In Ni-7Ti-X ternary alloys, surface appearance and microstructure were similar to Ni-7Ti binary alloys, and pitting and intergranular corrosion were also occurred in nitrided layers.

In Ni-7Ti-3Al alloy, there were precipitations which seemed to be γ' (Ni_3Al) type one in nitrided layer, because it contained alloying elements of both Ti and Al up to the solubility limit. Uniform corrosion was observed in Ni-7Ti-3Al and localized corrosion was not occurred.

On the contrary, corrosion behavior of Ni-20Cr-X ternary alloys were much different with Ni-20Cr binary alloy, though these were more changes in corrosion behavior caused by the kind of second alloying element "X". Uniform corrosion was shown in each Ni-20Cr-X ternary alloys and there were no pitting and intergranular corrosion, and moreover, no corrosion cavity was observed in nitrided layer of these Ni-20Cr-X ternary alloys.

3.3 Assessment of PIN treatable Ni alloys

Taking into consideration of surface hardness and thickness of nitrided layer, Ni-7Ti showed the highest surface hardness and the thickest nitrided layer in Ni binary alloys as shown in the previous report. Moreover, deterioration of corrosion resistence of Ni-7Ti alloy caused by PIN treatment was much lower than that of 18Cr-8Ni and these was no spalling of nitrided layer. In Ni-7Ti-X ternary alloys, there were few effect of second alloying elements on corrosion resistance of Ni-7Ti alloy as well as the surface hardness and thickness of nitrided layer. Ni-20Cr-X ternary alloys showed the surface hardness of nitrided layer as high as Ni-7Ti, though its thickness was not so large. Moreover, nitrided Ni-20Cr-X ternary alloys showed the uniform corrosion of their surfaces without the spalling of nitrided layer which was observed in nitrided Ni-30Cr and 20Cr binary alloys. In addition, anodic polarization current density of nitrided Ni-20Cr-X alloys was much lower than Ni-7Ti binary and ternary alloys, which showed the superior corrosion resistance of Ni-20Cr-X alloys.

Consequently, according to the experimental results in this study, it is considered that Ni-7Ti and Ni-7Ti-X alloys and Ni-20Cr-X ternary alloys are selected as the most beneficial alloys for PIN treatable Ni alloy.

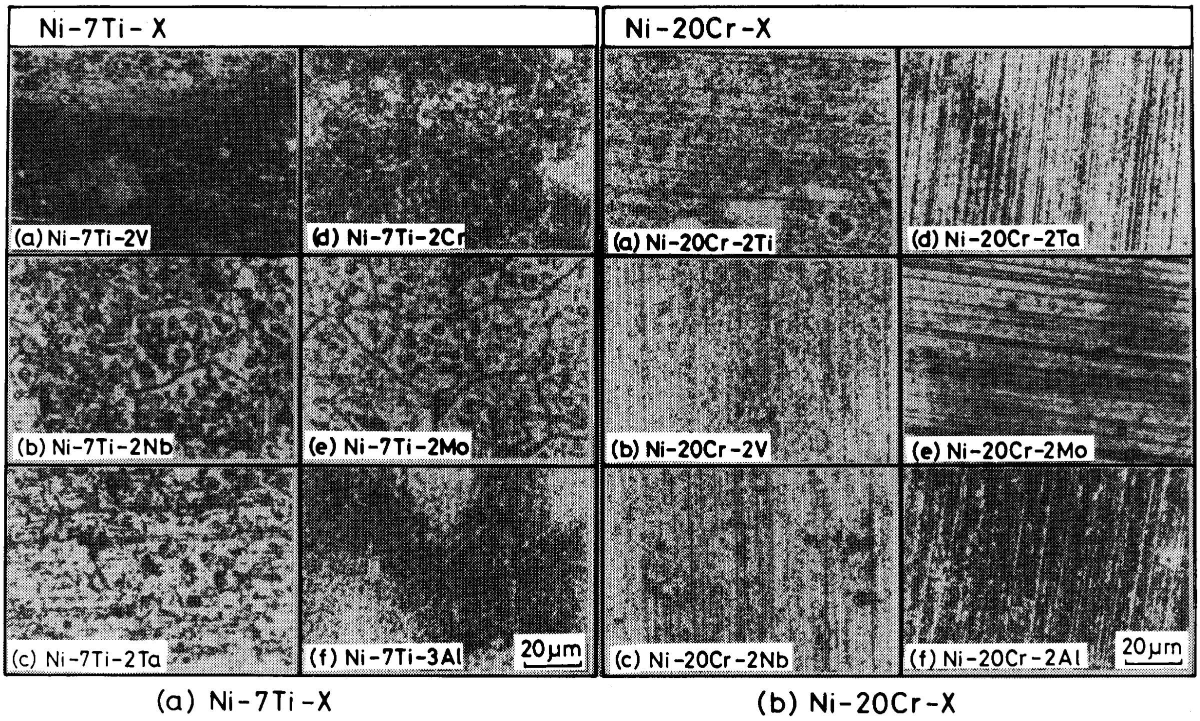

Fig. 7 Surface appearance of nitrided Ni ternary alloys after anodic polarization analysis

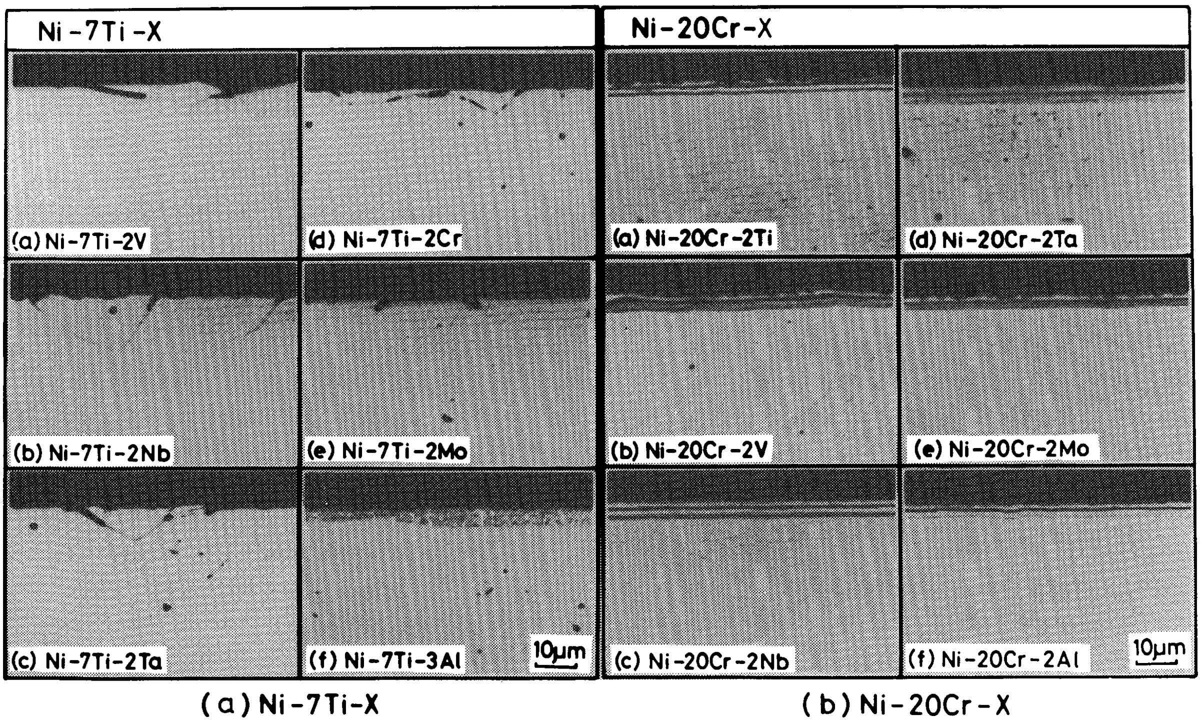

Fig. 8 Microstructure on crosssection of nitrided Ni ternary alloys after anodic polarization analysis

4. Conclusions

The effect of nitriding treatment by plasma ion nitriding (PIN) process on the anodic polarization properties and corrosion behavior of nitrided layer on tentative Ni binary alloys of Ni-7wt%Ti, -15wt%V, -10wt%Nb, -20wt%Cr and -30wt%Cr and Ni ternary alloys of Ni-7wt%Ti-2wt%(V, Nb, Ta, Cr, Mo or Al) and Ni-20wt%Cr-2wt%(Ti, V, Nb, Ta, Mo or Al) has been examined by potentiodynamic polarization methode. As a result, the following conclusions were obtained,

(1) Tentative Ni binary and ternary alloys showed typical polarization curve that indicated active, passive and transpassive regions in both untreated and nitrided conditions. Anodic current density of untreated Ni binary alloys were less than pure Ni except for Ni-15V. Ti, Nb and Cr were the effective alloying elements for corrosion resistance of Ni alloys.

(2) Anodic ploarization current density of tentative Ni alloys excepting Ni-15V were increased by PIN treatment, but it was lower than pure Ni and in addition, much lower than nitrided 18Cr-8Ni steel. Therefore, corrosion resistance of nitrided tentative Ni alloys was much superior than nitrided 18Cr-8Ni steel

(3) From the results of observation of surface appearance and crosssection in nitrided Ni alloys after measurement of anodic polarization curve, nitrided Ni binary and Ni-7Ti-X ternary alloys showed both the uniform corrosion and the localized corrosions of pitting and intergranular corrosion. Spalling of nitrided layer were observed in nitrided Ni-Cr binary alloys caused by the formation of corrosion cavity due to the preferential corrosion of inner zone of nitirded layer.
On the contrary, Ni-20Cr-X ternary alloys showed only uniform corrosion after PIN treatment, and the localized corrosion and spalling of nitrided layer was not occurred.

(4) Taking into consideration of anodic polarization properties, corrosion resistance, hardness and thickness of nitrided layer, Ni-7Ti binary alloy and Ni-7Ti-X and Ni-20Cr-X ternary alloys are considered to be the most beneficial Ni alloy for surface hardening by PIN treatment.

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