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Surface Hardening of Ni Alloys by Means of Plasma Ion Nitriding (PIN) Process (Report II)†
—Effect of Alloying Elements on Surface Hardening—

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Abstract

Tentative Ni binary alloys containing nitride forming elements such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Al and Si were nitrided by PIN process under the conditions of 873K, 10.8ks, N_2+H_2 mixed gas atmosphere of 800 Pa.

Surface hardening was observed in all Ni alloys used, however surface hardness was much different with depending on the kind of alloying element and its contents. Maximum surface hardness was approximately Hv550~800 for Ti, V, Nb and Cr containing alloys with more than 4, 4, 10 and 20wt%, respectively, and Hv300~400 for Mo, Fe and Mn containing alloys more than 20, 30 and 30wt%, respectivery, but Zr, Hf, Ta, Al and Si containing alloys were slightly hardened at Hv200~300. By using hardness increasing rate of each alloying elements, an equation to estimate the surface hardness of Ni alloy after PIN treatment was drawn and it was confirmed that there was a good agreement between measured and estimated hardness for various kinds of commercially used Ni alloys.

From results of EPMA and X-ray diffraction analyses, it was considered that surface hardening was due mainly to lattice strain of a matrix of nitrided layer caused by dispersive precipitations of fine nitride of each alloying elements.

KEY WORDS : (Plasma Nitriding) (Ion Nitriding) (Nitriding) (Nickel Alloy) (Surface Hardening) (Nitride)

1. Introduction

In the previous paper[1], the feasibility of the surface hardening of nickel (Ni) alloy by means of Plasma Ion Nitriding (PIN) process was investigated for various commercially-used Ni alloys. As a result, it was made clear that the alloys containing nitride forming elements such as Cr, Mo, Fe, Ta, and/or Al were possible to be hardened by PIN process, but pure-Ni and alloys with no nitride forming element were not hardened. Surface hardness of these alloys depended on the kind of alloying element and its content.

However, individual effect of alloying elements on surface hardening of Ni alloys has not been clear, because various nitride forming elements were contained with complex combination in commercially used Ni alloys.

Therefore, in this paper, individual effect of nitride forming element on surface hardening of Ni alloys by PIN process has been investigated by using tentative Ni binary alloys containing nitride forming element of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Al and Si, and benefitial alloying element and its comparison for surface hardening of Ni alloy have been examined. Moreover, surface hardening mechanism of Ni alloys by PIN treatment has been discussed mainly with X-ray diffraction analysis and X-ray probe microanalyzer (EPMA).

2. Experimental Procedure

2.1 Materials used

Thirty-one kinds tentative Ni binary alloys, which were contained nitride forming element of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Al and Si up to the solubility limit for each element, were prepeared with high frequency induction melting in argon atmosphere. These alloys were rolled at 1273K after casting and then annealed at 1173K for 10.8ks. Chemical compositions of these alloys were shown in **Table 1** where base metal hardness after PIN treatment and the solid solubility of each alloying element were also shown.

Moreover, eight kinds of commercially used Ni alloys were also used for comparison, of which chemical compositions are shown in **Table 2**.

Specimen size for PIN treatment was 10mm in width × 20mm in length × 3mm in thickness. A specimen surface was polished by emery paper up to ♯1200 and degreased with acetone before PIN treatment.

2.2 Plasma ion nitriding process

Figure 1 shows a shematic illustration of PIN apparatus and specimen arrangement used in this experiment. The

Table 1 Chemical compositions of tentative Ni binary alloys

Alloying element	Alloy	Content of alloying element(wt%)	Hardness (Hv)	Solid solubility in Ni(wt%)(temp.)
Ti	1Ti	1.10	130	7'(873K)
	1.5Ti	1.56	130	
	4Ti	3.69	150	
	7Ti	7.19	180	
Zr	0.3Zr	0.23	120	0.5 (293K)
Hf	1Hf	0.76	125	<0.5
V	1V	1.01	130	15 (873K)
	5V	5.01	150	
	10V	9.87	180	
	15V	14.87	260	
Nb	1Nb	1.25	140	9 (1073K)
	4Nb	3.89	170	
	10Nb	9.97	200	
Ta	1Ta	0.98	130	4 (873K)
	3Ta	2.86	140	
	5Ta	4.97	160	
Cr	5Cr	5.29	130	32 (823K)
	10Cr	10.60	140	
	15Cr	15.10	140	
	20Cr	20.54	150	
	30Cr	29.15	160	
Mo	5Mo	4.86	150	22 (873K)
	10Mo	9.89	170	
	20Mo	17.70	190	
Mn	10Mn	10.07	140	38 (873K)
	30Mn	29.70	170	
Fe	10Fe	10.41	130	74 (873K)
	20Fe	20.82	140	
	30Fe	33.12	160	
Al	6Al	5.68	170	7 (1073K)
Si	5Si	4.86	150	5 (873K)

PIN apparatus was the same as that in the previous work[1]. The parameter of the PIN treatment is nitriding gas composition, nitriding gas pressure, nitriding temperature and nitriding time. In order to examine effect of alloying element on the surface hardness after PIN treatment, these PIN parameters were 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 maximun value for each alloy according to a preliminary experiment.

After PIN treatment, surface hardness of each specimen was measured with microvickers hardness tester with 0.1N load. Microstructure of the surface hardened layer were observed on the crosssection of each specimen by an optical microscope after electorolytically etching with 10% oxialic acid solution. The composition of alloying element and nitrogen in a nitrided layer was measured by EPMA and the kind of the nitride precipitated there was identified by X-ray diffraction analysis with Cukα radiation (40kV, 20mA).
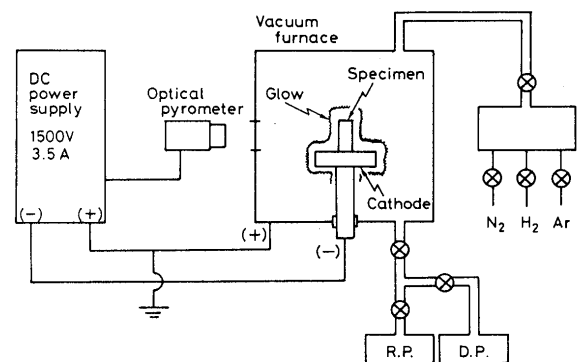

Fig. 1 Schematic illustration of Plasma Ion Nitriding (PIN) apparatus used

Table 2 Chemical compositions of commercially used Ni alloys and pure Ni

Alloy	Chemical Composition (wt%)															
	C	Mn	Si	Cr	Ni	Co	Mo	Nb	Ta	Fe	Ti	Al	Zr	V	Cu	W
Inconel 600	0.04	–	0.2	15.8	bal	–	–	–	–	7.2	–	–	–	–	–	–
Inconel 625	0.02	0.2	0.4	21.6	bal	–	8.3	3.7		2.6	0.2	0.1	–	–	–	–
Inconel 713C	0.12	–	–	12.5	bal	–	4.2	2.0	–	2.5	0.8	6.1	0.1	–	–	–
Udimet 500	0.09	–	–	18.8	bal	16.7	3.5	–	–	0.2	3.0	3.0	–	–	–	–
Hastelloy B	–	–	–	0.01	bal	0.8	27.0	–	–	4.8	–	–	–	0.03	–	–
Hastelloy C	–	–	–	15.5	bal	–	16.0	–	–	5.5	–	–	–	–	–	–
Hastelloy G	–	–	–	22.0	bal	–	6.5	2.0	–	19.5	–	–	–	–	2.0	4.0
Permalloy	–	–	–	–	bal	0.1	4.3	–	–	15.5	–	–	–	–	–	–
Pure Ni	–	–	–	–	99.96	–	–	–	–	–	–	–	–	–	–	–

3. Results and Discussions

3.1 Effect of alloying element on surface hardness

Figure 2 shows relation between the maximum surface hardness and the content of each alloying element (alloying content) after PIN treatment. Hardness of Ni in Fig.2 represents surface hardness of pure nickel after PIN treatment, about Hv130. Surface hardening was observed in all alloys used, however surface hardness was much different with depending on the kind of alloying element and its content. Approximately a linear relationship was obtained between surface hardness and the alloying content for each alloy system. Remarkable surface hardening was observed in the alloys containing Ti, V, Nb or Cr with more than 4, 4, 10 and 20Wt%, respectively. Mo, Fe or Mn containing alloys showed Hv300 ~ 400 of surface hardness with more than 20, 30 and 30wt%, respectively. On the contrary, Zr, Hf, Ta, Al or Si containing alloys were slightly hardened as Hv200~300 of the surface hardness.

A gradient of each line in Fig.2 represents a hardness increasing rate to the alloying content, $\Delta Hv/wt\%$; Hv = Maximum hardness − Core hardness, which means the hardenability of each alloying element in nickel with PIN treatment. These values obtained for each alloying element were as follows ; Zr:260, Hf:105, Ti:100, Nb:50, V:40, Ta:30, Al:25, Cr:20, Si:15, No:10, Fe:7, Mn:4. From the group of alloying element in periodic table, the most effective element for surface hardening of Ni alloys was IVa families followed Va, (VIa, IIIb, IVb) and (VIIa, VIII) families. Taking into consideration the hardness increasing rate and the maximum surface hardness for each alloy, it is considered that Ti, V, Nb and Cr are the most effective alloying element for the surface hardening of Ni alloys with PIN treatment. On the contrary, it is considered that Zr, Hf, Ta, Al and Mo, Fe, Mn are not effective alloying elements, because the former four elements have low solid solubility in nickel in spite of the comparably high hardness increasing rate and the latter three show low hardness increasing rate.

The hardness increasing rate of each alloying element was compared with the activation free energy of the formation of metal nitride for each alloying element at 873K[2]. These results were shown in Fig.3. There was an approximate relationship between the hardness increasing rate and the activation free energy, and the hardness increasing rate was increased with the activation free energy, although that of Al contained alloy somewhat lower even for their high activation energy. Therefore, this suggests that the alloying elements which easily formed the nitride show high hardness increasing rate.
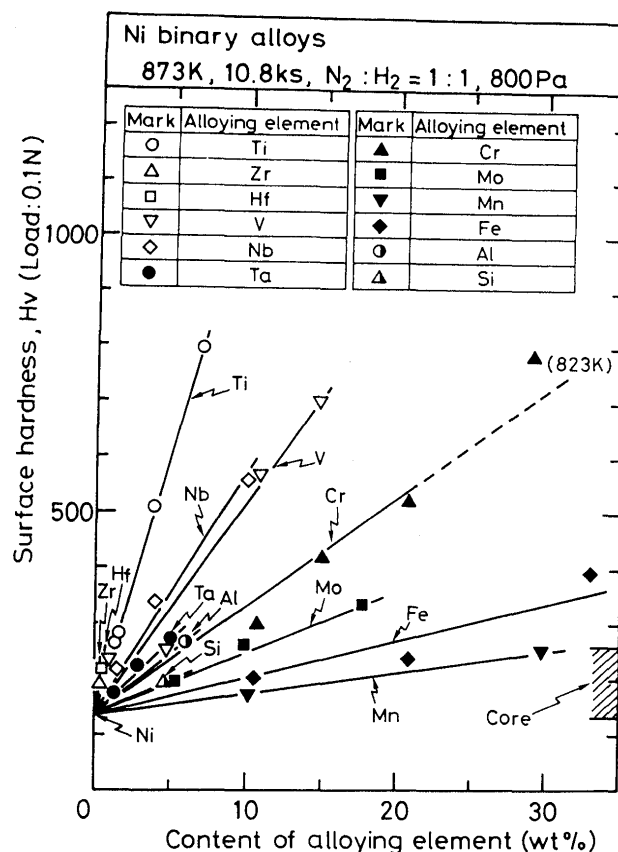

Fig. 2 Effect of alloying content on surface hardness of Ni binary alloys after PIN treatment
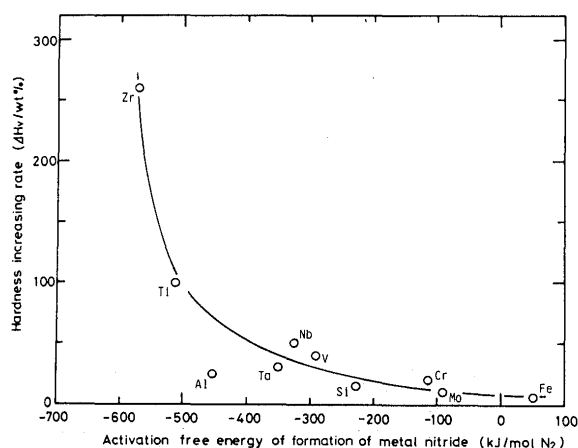

Fig. 3 Relation between hardness increasing rate and activation free energy of formation of metal nitride

3.2 Estimation of surface hardness of Ni alloys after PIN treatment

By using the hardness increasing rate obtained from Fig.2, an equation for estimating the surface hardness of Ni alloys after PIN treatment was drawn as equation (1) on the assumption that the effect of each alloying element on surface hardness can be additive without mutual effect.

$$(H_{VS})_E = 260[Zr] + 105[Hf] + 100[Ti] + 50[Nb] + 40[V]$$
$$+ 30[Ta] + 25[Al] + 20[Cr] + 15[Si] + 10[Mo] +$$
$$7[Fe] + 4[Mn] + 130 \ (\pm 15\%) \qquad (1)$$

where; $(Hvs)_E$: estimated surface hardness by eq.(1),

[element] : content of alloying element in wt%

numerical coefficients : hardness increasing rate of each element as mentions in 3.1.

130 of last term : the surface hardness of pure Ni after PIN treatment

the value of $(\pm 15\%)$: hardness allowance

Eq.(1) should be applied to estimate the surface hardness under the conditions of nitriding temperature at 873K, nitriding time for 10.8ks and treated gas N_2 : $H_2 = 1$: 1, 800Pa.

The applicability of eq.(1) was examined by using the data measured on 8 kinds of commercially used Ni alloys after PIN treatment. **Figure 4** shows the relation between the surface hardness estimated by eq.(1) and the surface hardness measured. The range between two solid lines in Fig.4 is the applicable range of eq.(1) $(\pm 15\%)$. As a result, there is a good agreement between hardness estimated and hardness measured, although the hardness measured of Inconel 600 and 713C showed slightly higher than the hardness estimated. Consequently, it was made clear that the eq.(1) is applicable to estimate the surface hardness after PIN treatment for Ni alloys which complexly contained various alloying elements.

3.3 Microstructure of nitrided layer

Figure 5 shows the microstructures of nitrided layer by electroliticaly etched with 10% oxialic acid solution on the crosssections of Ni binary alloys containing maximum content of alloying element. A nitrided layer was clearly observed in Ni-Ti, -V, -Nb, -Cr and -Mn binary alloys, and there were two types of nitrided layer, one was a single layer as observed on Ni-Ti, -Nb and -Mn alloys, and the other was double layer as observed on Ni-V and -Cr alloys. On the contrary, nitrided layer was not observed in Ni-Zr, -Hf, -Ta, -Mo, -Mn, -Fe, -Al and -Si alloys, but grain boundaries near the surface of specimen became appeared in these alloys instead of nitrided layer. Moreover, these grain baundaries were also observed even in the nitrided layers of Ni-V, -Nb and -Cr alloys. Therefore these three alloys seem to be an intermediate type. From the results of the microstructural observation of Ni binary alloys as Fig.5 and commercially-used Ni alloys in the previous work[1], it is made clear that the Ni alloys with the obvious nitrided layer showed remarkable surface hardening by PIN treatment, but the alloys with no nitrided layer were slightly hardened.
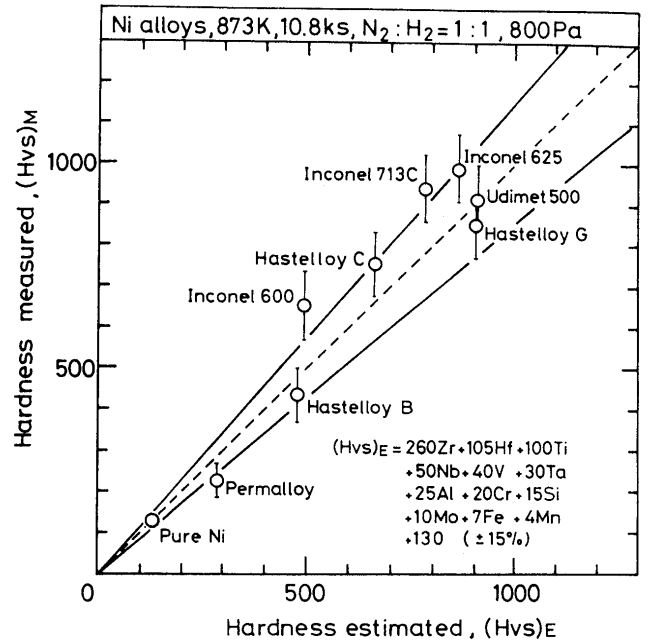
Figure 6 shows the relation between the thickness of

Fig. 4 Relation between hardness estimated $(Hvs)_E$ and hardness measured $(Hvs)_M$ for commercially used Ni alloys and pure Ni
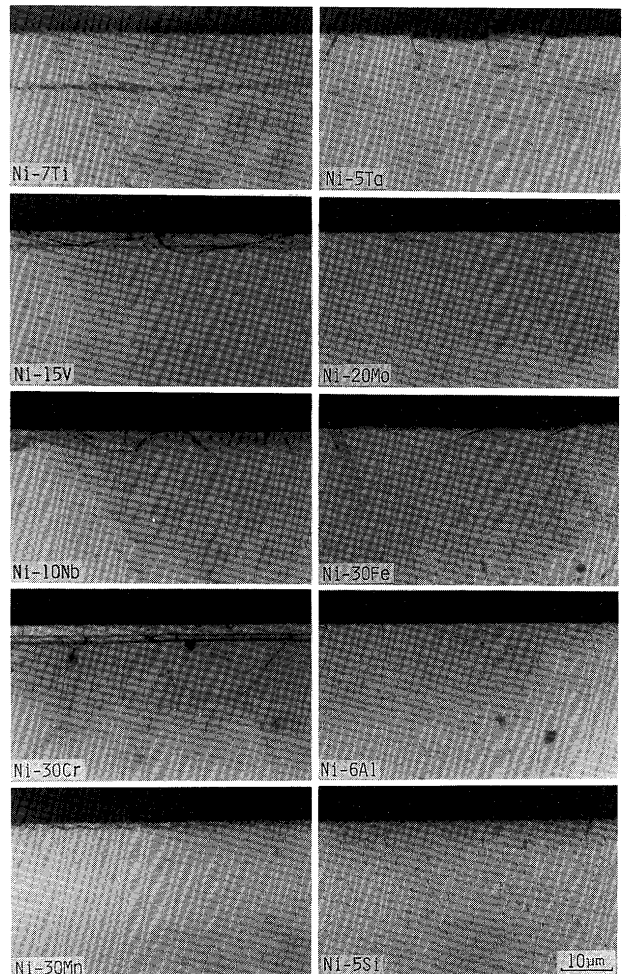

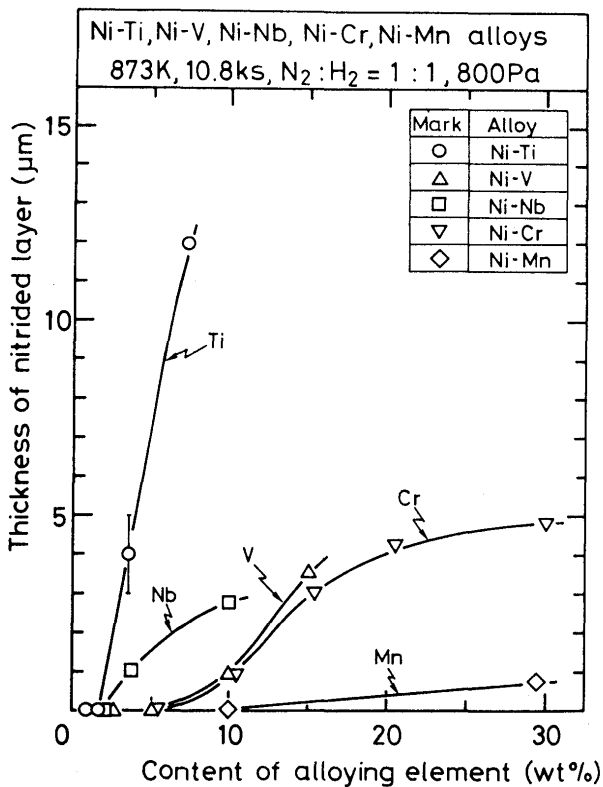Fig. 5 Microstructure on crosssections of Ni binary alloys after PIN treatment at 873K for 10.8ks

Fig. 6 Effect of alloying element on thickness of nitrided layer

nitrided layer and the content of alloying element in Ni-Ti, -V, -Nb, -Cr and -Mn alloys. The nitrided layer was observed with the alloying content more than 4, 4, 10, 10 and 30wt% for Ni-Ti, -Nb, -V, -Cr and -Mn alloys, respectively. The thickness of nitrided layer of Ni-Ti alloys increased linearly with the increase in Ti content and was much thicker than those for the other alloy systems. Those of Ni-V, -Nb and -Cr alloys systems increased with the increase in alloying content, but they were likely to saturate to about $3 \sim 5\ \mu$m even with the maximum content near the solid solubility in nickel for each element. Ni-Mn alloy showed only a thin nitrided layer, about 1 μm or less even with much content, 30wt%. Consequently, it is made clear that titanium is the most effective alloying element for the surface hardening by PIN treatment to make a thick and hard nitrided layer.

3.4 EPMA analysis of nitrided layer

In order to examine the composition of the nitrided layer, nitrogen and each alloying element in the nitrided layer were analyzed with EPMA. **Figure 7 (a) and (b)** shows the typical results of EPMA together with the SEM microphotograph in upper side in figure for Ni-7Ti and -30Cr alloys which were the typical alloys showing single and double nitrided layers, respectively. Nickel was electorolytically plated on the surface of specimen after PIN

treatment to protect the detail of the specimen surface.

Nitrogen concentrated only in the nitrided layer. The distribution of nitrogen in nitrided layer of Ni-7Ti was almost constant through the nitrided layer, but for Ni-30Cr, it was not uniform in the nitrided layer, that is, nitrogen content in a outer layer was high, but in a inner layer was low. On the contrary, there was no different in the contents of Ni and alloying elements, Ti and Cr between the nitrided layer and base metal for each alloy.

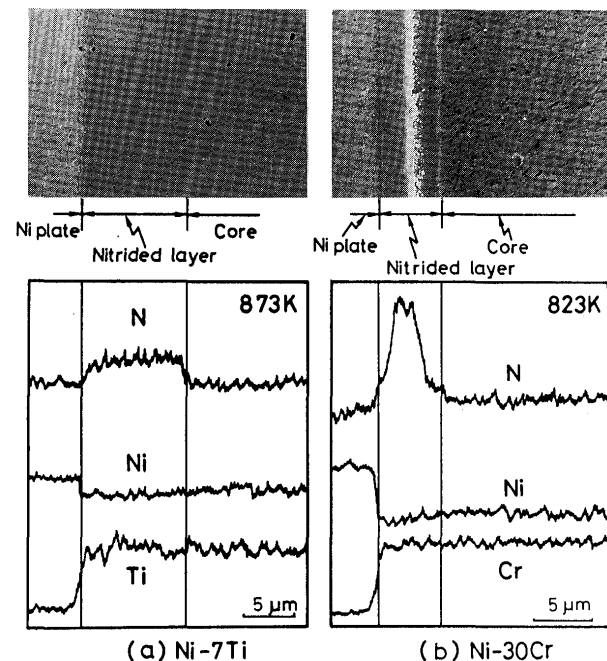These results suggest that the nitrided layer is not

Fig. 7 Distribution of N, Ni, Ti and Cr in nitrided layer of Ni-7Ti (a) and Ni-30Cr (b)

composed of the nitride only, but it is formed as the layer which the nitride precipitated dispersively in alloy matrix or nitrogen concentrated in alloy matrix.

Almost the same distributions of nitrogen and alloying elements were observed in the nitrided layer of Ni-V, -Nb and -Mn alloys. On the contrary, only slight concentration of nitrogen near the surface of the specimen was observed in other alloys with no nitrided layer.

3.5 X-ray diffraction analysis

X-ray diffraction analysis for the specimen surface after PIN treatment was carried out to identified the kind of the nitride precipitated in the nitrded layer. **Figure 8 (a)** to **(l)** shows the X-ray diffraction pattern of each Ni binary alloys containing maximum alloying content for each alloy system, and identified phases for each alloys are listed in **Table 3** together with the observation results about the formation of the nitrided layer on crosssection. The diffraction peak hight of the identified phase in the
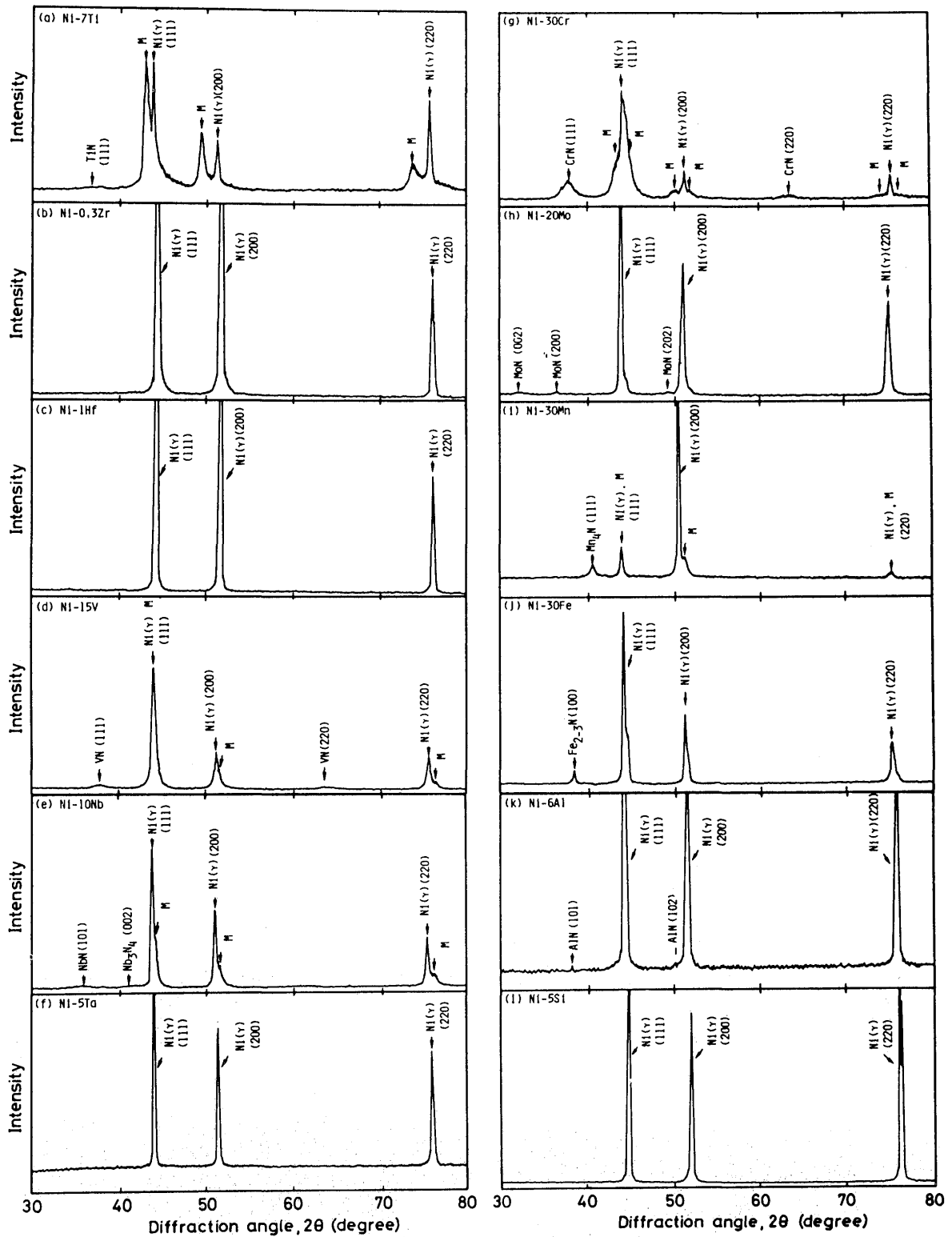
Fig. 8 X-ray diffraction pattern of surface of specimens after PIN treatment : (a) Ni-7Ti, (B) Ni-0.3Zr, (c) Ni-1Hf, (d) Ni-15V, (e) Ni-10Nb, (f) Ni-5Ta, (g) Ni-30Cr (h) Ni-20Mo, (i) Ni-30Mn, (j) Ni-30Fe, (k) Ni-6Al, (l) Ni-5Si

Table 3 List of phases detected with X-ray diffraction analysis
of Ni binary alloys after PIN treatment

Alloy	Identified phase			Nitrided layer *
1Ti	Ni(γ)	—	—	x
1.5Ti	Ni(γ)	—	—	x
4Ti	Ni(γ)	M	TiN	o
7Ti	M	Ni(γ)	TiN	o
0.3Zr	Ni(γ)	—	—	x
1Hf	Ni(γ)	—	—	x
1V	Ni(γ)	—	—	x
5V	Ni(γ)	—	—	x
10V	Ni(γ)	M	VN	o
15V	Ni(γ)	M	VN	o
1Nb	Ni(γ)	—	—	x
4Nb	Ni(γ)	M	NbN	o
10Nb	Ni(γ)	M	NbN,Nb$_3$N$_4$	o
1Ta	Ni(γ)	—	—	x
3Ta	Ni(γ)	—	—	x
5Ta	Ni(γ)	—	—	x
5Cr	Ni(γ)	—	—	x
10Cr	Ni(γ)	M	CrN	o
15Cr	Ni(γ)	M	CrN	o
20Cr	Ni(γ)	M	CrN	o
30Cr	Ni(γ)	M	CrN	o
5Mo	Ni(γ)	—	—	x
10Mo	Ni(γ)	—	—	x
20Mo	Ni(γ)	—	MoN	x
10Mn	Ni(γ)	—	Mn$_4$N	x
30Mn	Ni(γ)	M	Mn$_4$N	o
10Fe	Ni(γ)	—	Fe$_{2-3}$N	x
20Fe	Ni(γ)	—	Fe$_{2-3}$N	x
30Fe	Ni(γ)	—	Fe$_{2-3}$N	x
6Al	Ni(γ)	—	AlN	x
5Si	Ni(γ)	—	—	x

*) o : Observed, x : Not observed on
crosssection of treated specimen

left side in Table 3 is higher than those of the right side
phase.

Three types of the diffraction peaks were observed in
these analyses, that is, Ni(γ), nitride of each alloying ele-
ment and 'M', which were observed in the case of com-
mercially-used Ni alloys as reported in the previous
paper[1]. Ni(γ) was the peak of the base metal beneath
the nitrided layer.

Nitrides were identified in Ni-Ti, -V, -Nb, -Cr, -Mo, -
Mn, -Fe and -Al alloys with its alloying content more than
4, 10, 4, 10, 20, 10, 10 and 6 wt%, respectivery, but was
not identified in Ni-Zr, -Hf, -Ta and -Si alloys. Taking

into consideration the activation free energy of the forma-
tion of metal nitride for each alloying element, the nitride
of Zr, Hf, Ta or Si should be formed at this nitriding
temperature. The reason why those nitride were not de-
tected in this analysis was considered that the amount of
the nitride of those elements precipitated was very small
owing to small alloying content of those alloys. Therefore,
these nitrides were not able to be detected with X-ray dif-
fraction analysis.

It seems that the reason why nitrides were not de-
tected in Ni-Ti, -V, -Nb, -Cr and -Mo alloys with each
alloying content less than 1.5, 5, 1, 5 and 10wt%, respec-
tively was also owing to small alloying content of these
alloys. Moreover, the existance of the nitride detected by
X-ray diffraction not always means the formation of the
nitrided layer.

On the contrary, a close relationship was observed be-
tween M phase and the formation of the nitrided layer.
That is, it was identified only the alloys with the obvious
nitrided layer in Ni-Ti, -V, -Nb, -Cr and -Mn alloy sys-
tems, but not identified in the alloys with no nitrided
layer. The phase shown as 'M' was not detected in ASTM
Powder Diffraction File. The diffraction peaks of 'M'
were observed near each peaks of base metal,(γ).
Moreover, one diffraction peak of M phase was observed
corresponding to each peak of Ni(γ) of the base metal in
the alloys showing the single nitrided layer such as Ni-Ti
and -Nb alloys, and two diffraction peaks of M phase
were observed corresponding to each peak of Ni(γ) of
the base metal in the alloys showing the double nitride
layer such as Ni-V and -Cr alloys. Therefore, it was consi-
dered that M phase has the same crystal structure as the
base matel of each alloy. As mentions in 3.4, it was consi-
dered that nitrided layer was formed as the layer which
nitride precipitated in alloy matrix.

Therefore, the results of EPMA and X-ray diffraction
analysis clearly indicate that M phase is a matrix of nit-
rided layer in which fine nitrides precipitated dispersively.

Remarkable broadening of the widths of diffraction
peaks of nitride and M phase was observed in the alloys
which showed obvious surface hardening. Therefore, it is
considered that the broadening of diffraction peaks of
both nitride and matrix of nitrided layer were concerned
with surface hardening.

In general, the broadening of width of X-ray diffrac-
tion peaks means that the grain size of crystal is very
small or uneven microstrain exists in crystal lattice[3].
Moreover, it is also well known that this uneven micros-
train causes the surface hardening of crystal[4]. The surface
hardness of the alloys with the obvious nitrided layer, Ni-
Ti, -V, -Nb and -Cr alloys is shown in **Fig.9** as the func-
tion of the half value width (Δ2 θ) of the diffraction

peaks of the matrix of nitrided layer which was selected as the one corresponding to the base metal peak, γ (220). The data of commercially-used Ni alloys obtained in the previous paper[1] were also shown as the dashed line in Fig.9.

As a result, it was made clear that there was a good relationship between the surface hardness and $\Delta 2 \theta$. Namely, surface hardness of Ni alloys was almost linearly increased with the increase in the half value width of the matrix of nitrided layer, although some scattering range in data was observed in Fig.9. Therefore, it is considered that the surface hardening of Ni binary alloys by PIN treatment was due mainly to microstrain in the matrix of the nitrided layer caused by dispersive precipitations of fine nitride. These results also indicate that the nitride precipitated to have the coherency with the nitrided layer matrix 'M' and caused an uneven microstrain in the nitrided layer matrix around the precipitated nitride perticle. The broadening of diffraction peaks of nitride means either very fine grain size of nitride or the coherency of nitride with the matrix, but it was not clear that it means the fine nitride size or the nitride and having coherency with matrix. The coherency between the nitride and nitrided layer matrix will be discuss with transmittion electron microscope (TEM) analysis in the following paper.

Figure 10 shows the effect of the alloying content on the half value width of M(220) in Ni-Ti, -V, -Nb and -Cr

alloys. The half value width was almost linearly increased with the alloying content for each alloy. The increasing rate of the half value width to the alloying content for Ni-Ti system is much larger than the other elements, and the order of the increasing rate of the half value width is as follows; Ti > Nb > V > Cr. This order is the same as the order in the increasing rate of the surface hardness in Fig.2. Therefore, the effective alloying element for the surface hardening of Ni alloys is that which induces large microstrain in the matrix of the nitrided layer with the precipitation of its fine nitride even with small alloying content such as Ti. However, the reason about the large difference in the microstrain between each alloying element has not been made clear in this paper.

3.6 Mechanism of the formation and the hardening of nitrided layer

According to the experimental results in this study, the composition of the nitrided layer of Ni alloy after PIN treatment can be drawn schematically as **Fig.11.** The formation of nitrided layer was considered as followed;

(i) Surface reaction process

Nitrogen or nitrogen-hydrogen ions were accelereted in cathode full region by glow discharge and came into collision with specimen surface, and then nitrogen penetrated into specimen. However, there is two kinds of nitrogen penetration mechanism as follows ;
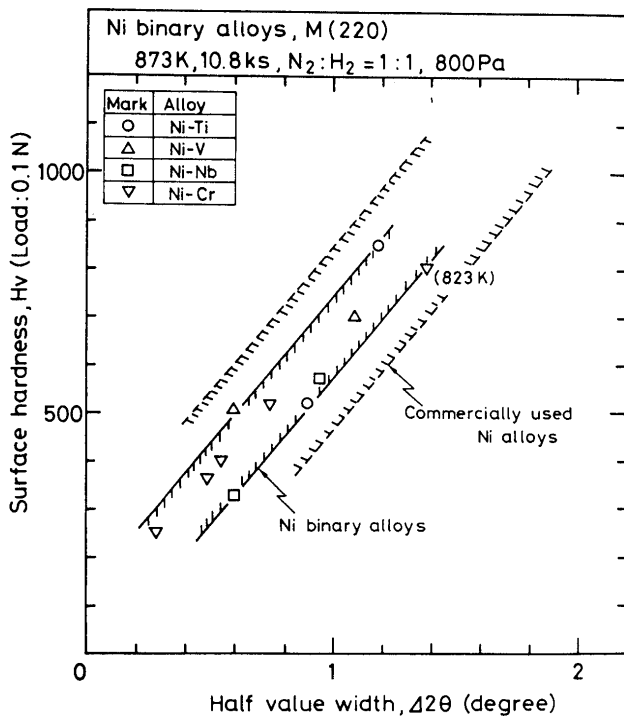

Fig. 9 Relation between surface hardness and half value width of X-ray diffraction peak of the matrix of nitrided layer, M(220)
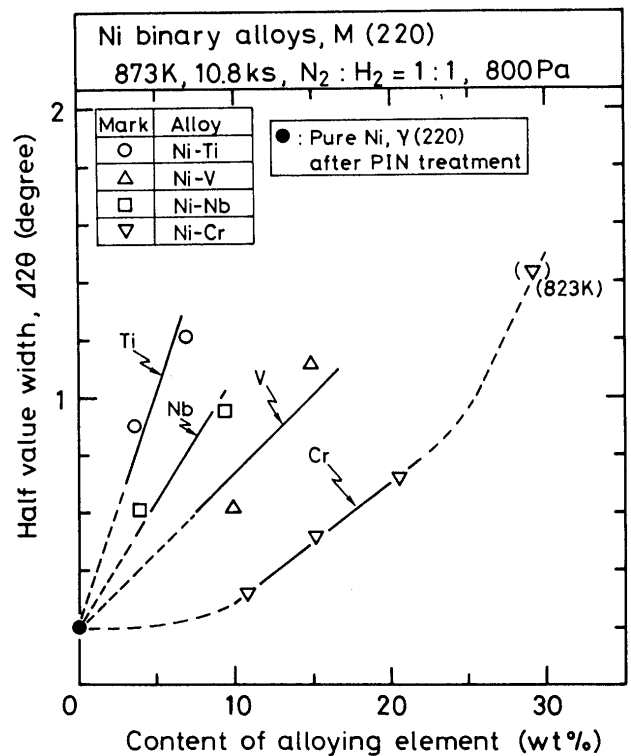

Fig. 10 Fffect of alloying content on half value width of X-ray diffraction peak of the matrix of nitrided layer, M(220)

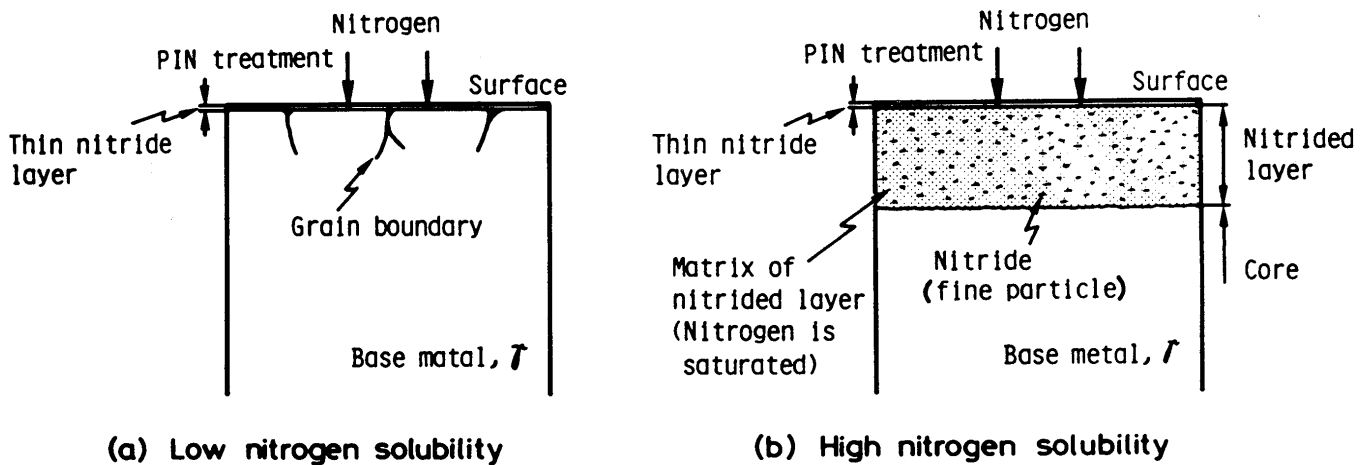(a) Low nitrogen solubility   (b) High nitrogen solubility

Fig. 11 Illustration of principle for the composition of the nitrided layer : (a) low nitrogen solubility, (b) high nitrogen solubility

① nitrogen penetrates directly from the specimen surface and diffused into specimen from atmosphere or

② nitrogen diffuses into the specimen through a thin nitride layer formed on the specimen surface.

From results of the previous paper[1], it is suggested that the thin nitride layer was formed on surface at the first stage of the PIN treatment. Therefore, it is considered that a latter mechanism (②) occurred at surface during PIN treatment. Moreover, it is considered that there are two kinds of formation mechanism of nitrided layer at the first stage of the PIN process, that is : (a) nitrogen combines directly with alloying element at specimen surface and form a thin nitride layer, or, (b) nitrogen combines with the nitride forming element sputtered from the specimen surface in atmosphere and form the nitride, which deposites on specimen surface and forms a thin nitrided layer on its surface. However, it was not clear in this paper, which mechanism are dominant.

(ii) Nitrogen diffusion process

Nitrogen diffuses into the interior of the alloy through the thin nitrided layer, but different diffusion processes of nitrogen may occur depending on the solubility of nitrogen in the alloy, that is :

① In case of the alloy with very little nitrogen solubility : nitrogen diffuses preferentially along the grain boundary. In this case, nitrided layer is not formed in alloys, but grain boundary precipitation of nitride occurs.

② In case of the alloy with high nitrogen solubility : nitrogen diffuses into the grains and combines with alloying element to form the nitride precipitation. That is so called the nitrided layer in this paper.

It is considered that the alloys showing grain boundary precipitation has little solid solubility of nitrogen in alloy matrix as Ni-Zr, -Hf, -Ta, -Mo, -Fe, -Al or -Si alloys and the alloys showing the nitrided layer has high solubility of

nitrogen in alloy matrix as Ni-Ti, -Cr or -Mn alloys. The alloys showing both nitrided layer and grain boundary as Ni-V or -Nb alloys seem to be an intermediate type.

(iii) Hardening process

In the nitrided layer, a fine nitrides having the coherence with the matrix is precipitated dispersively in a nitrogenous matrix of the alloy. These nitrides induced the uneven microstrain in the matrix of nitrided layer and this causes the hardening of the nitrided layer.

Therefore, the surface hardening of Ni alloys by PIN treatment was due mainly to an uneven microstrain in the matrix of nitrided layer.

4. Conclusions

Effect of alloying element on the surface hardening by PIN process was investigated by using 31 kinds of Ni binary alloys containing nitride forming elements of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Al or Si and 8 kinds of commercially used Ni alloys.

As a result, the following conclusions were obtained:

(1) All tentative Ni binary alloys were hardened by PIN process, however surface hardness was much different with depending on the kind of alloying element and its content. Surface hardness with more than Hv500 was obtained in Ti, V, Nb or Cr contained alloys, but Zr, Hf, Ta, Al, Si, Mo, Fe or Mn contained alloys showed surface hardness less than Hv400.

(2) Surface hardness was linearly increased with the alloying content. Hardness increasing rate for alloying content (ΔHv/wt%) was classified as followed:

IVa(Ti, Zr, Hf) > Va(V, Nb, Ta) > |IIIb(Al), VIa(Cr, Mo), IVb(Si)| > |VIIa(Mn), VIII(Fe)| .

It is considered that Ti, V, Nb and Cr were the effective alloying elements for the surface hardening of Ni alloys

with PIN process.

(3)   Nitrided layer was observed in alloys showing the remarkable surface hardening as Ni-Ti, -V, -Nb and -Cr alloys which contained alloying element more than 4wt% for Ni-Ti, -Nb and more than 10wt% for Ni-V, -Cr alloys. These nitrided layers were formed as the layer where nitride dispersively precipitated.

(4)   From the result of X-ray diffraction analysis, the nitride of each alloying element was detected in Ti, V, Nb, Cr, Mo, Mn, Fe or Al containing alloys, but was not detected in Zr, Hf, Ta, or Si containing alloys.

Diffraction peaks of the nitride and the matrix of nitrided layer in Ni-Ti, -V,-Nb and -Cr alloys were very broad and the half value width of the matrix of nitrided layer had a good correlation with the surface hardness, which was linearly increased as the increase of the half value width of the matrix of the nitrided layer.

Half value width of the matrix of nitrided layer increased with the alloying content and the order of increasing rate of half value width for alloying content was as follows ; Ti>Nb>V>Cr. This order has good agreement with the hardness increasing rate for the alloying content. It is considered that the hardness increase of Ni alloys with PIN process was due to the uneven microstrain in the nitrided layer induced by the precipitation of the nitride.

(5)   By using the hardness increasing rate for the alloying

content for tentative Ni binary alloys after PIN treatment, an equation to estimate the surface hardness of Ni alloys was drawn as follows :

$$(H_{vs})_E = 260[Zr] + 105[Hf] + 100[Ti] + 50[Nb] + 40[V] + 30[Ta] + 25[Al] + 20[Cr] + 15[Si] + 10[Mo] + 7[Fe] + 4[Mn] + 130$$
$$(\pm 15\%)$$

where $(Hvs)_E$: estimating surface hardness, Hv
  [element] : content of alloying element (wt%)
  PIN conditions: 873K, 10.8ks, 800Pa, $N_2/H_2 = 1/1$

The applicability of this equation was confirmed by estimating the surface hardness of 8 kinds of commercially used Ni alloy after PIN treatment.

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