



Title	Surface Hardening of Ni Alloys by Means of Plasma Ion Nitriding (PIN) Process (Report 1) (Materials, Metallurgy & Weldability)
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# Surface Hardening of Ni Alloys by Means of Plasma Ion Nitriding (PIN) Process (Report 1)<sup>†</sup>

Fukuhisa MATSUDA\*, Kazuhiro NAKATA\*\* and Takashi MAKISHI\*\*\*

## Abstract

*The probability of surface hardening by means of Plasma Ion Nitriding (PIN) process was investigated for pure nickel and commercially used Ni alloys under the conditions of nitriding temperature 773 to 1073K and nitriding time up to 32.4ks in N<sub>2</sub>+H<sub>2</sub> mixed gas atmosphere of 800Pa.*

*Remarkable surface hardening more than Hv500 was observed at nitriding temperature 733-1073K for Inconel 600, 625, 713C and Udimet 500 which contain chromium, and Hastelloy B which contains molybdenum. On the contrary, Permalloy which contains iron was slightly hardened, and pure Ni and Monel were not hardened.*

*From the result of X-ray diffraction analysis, CrN for Inconel 600, 625, 713C and Udimet 500, MoN and Mo<sub>2</sub>N for Hastelloy B were detected as nitrides together with diffraction peaks from the matrix of nitrided layer and base metal beneath it. Diffraction peaks of these nitrides and matrix of nitrided layer were very broad and the half value width of these peaks had a good relationship with surface hardness, which was linearly increased as the increase of the half value width.*

*Therefore, it was considered that hardness increase in PIN process of Ni alloys was due to ununiform microstrain caused by the precipitation of such nitrides in nitrided layer.*

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

## 1. Introduction

Nickel and its alloys are widely used for industrial materials, but industrial surface hardening process which enhance wear resistant for these materials has not been established so far. In general, there are two kinds of surface hardening processes, that is, a diffusion process such as carburizing, nitriding and boronizing for iron and steel, and a coating process such as CVD and PVD. Among these diffusion process only boronizing is a possible method for surface hardening of Ni<sup>1)</sup>. However, boronizing treatment has not been established as an industrial surface hardening process as carburizing and nitriding. On the other hand, hard ceramics coating such as TiN by CVD and PVD is applicable to any metals and alloys, but it is much more expensive than diffusion process.

On the contrary, Plasma Ion Nitriding (PIN) process assisted by glow discharge which is one of the nitriding processes is widely used in an industrial surface hardening process due to its beneficial features such as energy and

labour savings, good reproducibility of the property of nitrided layer and no requirement of anti-pollution equipment<sup>2)</sup>. Therefore, PIN process is applied not only to iron and steels but also to nonferrous metals such as titanium, zirconium and so on<sup>3)</sup>.

However, nitriding treatment has not been applied to Ni because the metals such as Ni, Co, Cu, Au or Ag which do not have the solubility of nitrogen and not form nitride can not be hardened by nitriding treatment<sup>4)</sup>.

It is well known that the typical nitride forming elements of IVa, Va, and VIa families in Periodic Table are easily hardened by nitriding treatment. So when some nitride forming elements are added in pure Ni, surface hardening of Ni alloy by nitriding may become possible, if the nitrogen diffuses into Ni alloy from its surface and reacts with alloying element to make their nitride near the surface of Ni alloy.

Therefore, in order to confirm this, as a preliminary investigation, the probability of surface hardening of Ni alloy by means of PIN process has been investigated by

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**Table 1** Chemical composition 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
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	-
Permalloy	-	0.5	-	-	bal	0.1	4.3	-	-	15.5	-	-	-	-	-
Monel	0.06	1.0	0.3	-	bal	-	-	-	-	0.7	-	-	-	-	32.1
Pure Ni	-	-	-	-	99.96	-	-	-	-	-	-	-	-	-	-

using some commercially-used Ni alloys, and moreover the effect of nitriding conditions on surface hardening and its mechanism has been also investigated by X-ray probe microanalyzer (EPMA) and X-ray diffraction analysis.

## 2. Experimental Procedure

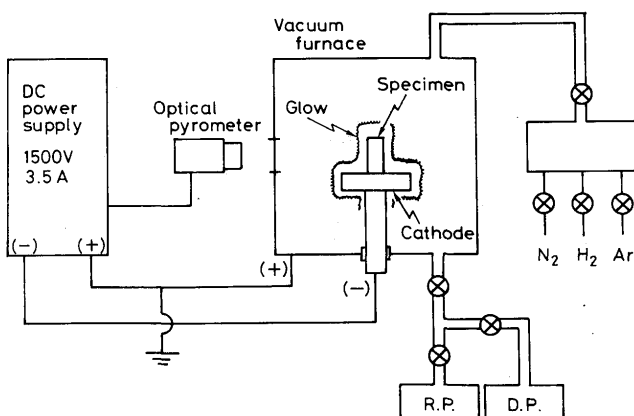
### 2.1 Materials used

Inconel 600, 625, 713C and Udimet 500 as Ni-Cr base heat resistant alloys, Hastelloy B as Ni-Mo and Monel as Ni-Cu base corrosion resistant alloys, Permalloy as Ni-Fe base magnet material and pure Ni are used in this investigation. Chemical compositions of these materials are shown in **Table 1**. All materials are commercially available.

All specimens were cut and machined from plates or bars to 10 x 20 x 3mm thickness or 10mm dia. x 20mm thickness and were polished by emery paper #1200 and degreased with acetone.

### 2.2 Plasma Ion Nitriding apparatus

**Figure 1** shows a schematic illustration of Plasma Ion



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

Nitriding (PIN) apparatus used in this experiment. A specimen is set on a cathode plate which is made of pure Ni in a vacuum chamber, and a dc glow discharge between a vacuum chamber wall as anode and a specimen as cathode was used for treatment. After the vacuum chamber was evacuated to a pressure of about 0.65Pa by mechanical pump, nitrogen and hydrogen mixed gas (nominal purity 99.9999%, 50vol%N<sub>2</sub> + 50vol%H<sub>2</sub>) was fed to the vacuum chamber to a constant pressure, 800Pa. Dc glow discharge was generated under a constant gas pressure. Nitriding temperature which was the specimen surface temperature measured by an optical pyrometer was kept constant by controlling a discharge voltage and varied from 773 to 1073K, and heating rate was about 40K/min and cooling rate was about 70K/min from each nitriding temperature to 673K. Nitriding time was also varied from 3.6 to 32.4ks.

After PIN treatment, surface hardness of each specimen was measured by using microvickers hardness tester with a 0.1N load. The crosssection of each specimens were observed by using an optical microscope after electrolytically etching using 10% oxalic acid solution. The compositions of alloying elements and nitrogen in nitrided layer which was not the nitride layer but the nitrogen diffusion layer where nitride dispersively precipitated as mentioned in 3.3 were determined by means of EPMA, and the kind of nitride was identified by X-ray diffraction analysis with Cu K $\alpha$  radiation.

## 3. Results and Discussions

### 3.1 Surface hardness

**Figure 2** shows the relation between surface hardness and nitriding temperature for pure Ni and Ni alloys. The core hardness in the figure shows the range of base metal hardness of each alloys after PIN treatment, that is, Hv100-370, and it was not varied by PIN treatment in nitriding conditions used for each alloy.

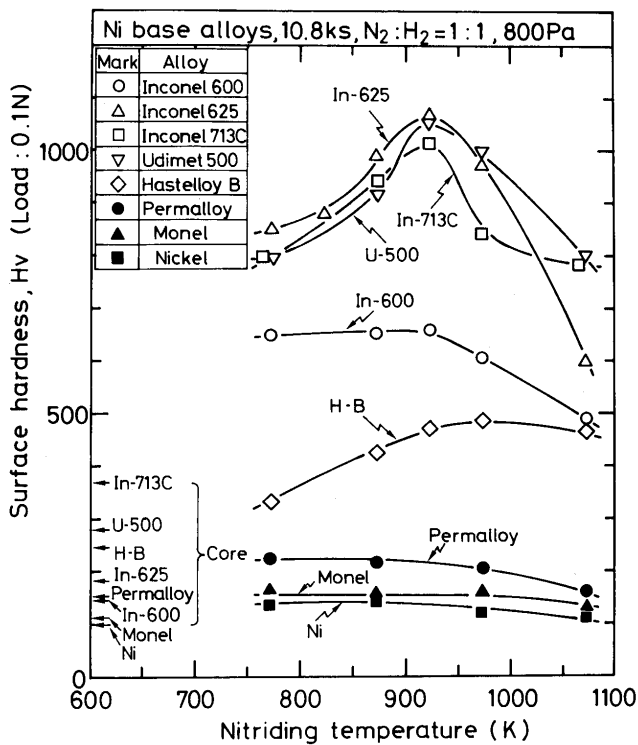


Fig. 2 Relation between surface hardness and nitriding temperature for Ni alloys and pure Ni

Remarkable surface hardening was observed for chromium contained Inconel 600, 625, 713C and Udimet 500, and molybdenum contained Hastelloy B at nitriding temperature 773-1073K and nitriding time more than 10.8ks. Surface hardness was much different on both kinds of alloy and nitriding temperature. Maximum surface hardness was observed at nitriding temperature 900-1000K for each alloy, and surface hardness of these alloys increased with an increase of nitriding temperature from 773 to 923K, but then it decreased with an increase in nitriding temperature more than 973K. The maximum surface hardness for each alloy was approximately Hv1000-1100 for Inconel 625, 713C and Udimet 500 (core hardness Hv180, 370 and 280, respectively), Hv650 for Inconel 600 (core hardness Hv150) and Hv500 for Hastelloy B (core hardness Hv250).

On the contrary, Permalloy containing iron was slightly hardened as Hv230. Almost no increase in surface hardness was observed in pure Ni and Monel, but only slight increase of about Hv30 in surface hardness in these materials was considered to be due to the formation of lattice imperfection into specimen surface region by ion bombardment<sup>5</sup>.

From these results, it is confirmed that several Ni alloys contained some nitride forming elements were possible to be hardened by PIN treatment, although pure Ni was not hardened. Taking into consideration the

composition of alloying elements in each alloy and their maximum hardness, it seemed that chromium was more effective alloying element to surface hardening of Ni alloy than molybdenum and iron. Copper as alloying element showed no effect because of non-nitride forming element.

Moreover, the reason of surface hardness change against nitriding temperature is considered as followed; lower hardness value at lower nitriding temperature than 873K was owing to very thin nitrided layer about 2-3 $\mu$ m at these temperature range. On the other hand, hardness decrease at higher temperature than 973K even with thicker nitride layer is considered owing to the decrease in ununiform microstrain caused by coarsening of nitride precipitated in nitrided layer<sup>6</sup>.

### 3.2 Microstructure of nitrided layer

Figure 3 (a) to (h) shows typical crosssectional microstructure of nitrided specimen near the specimen surface

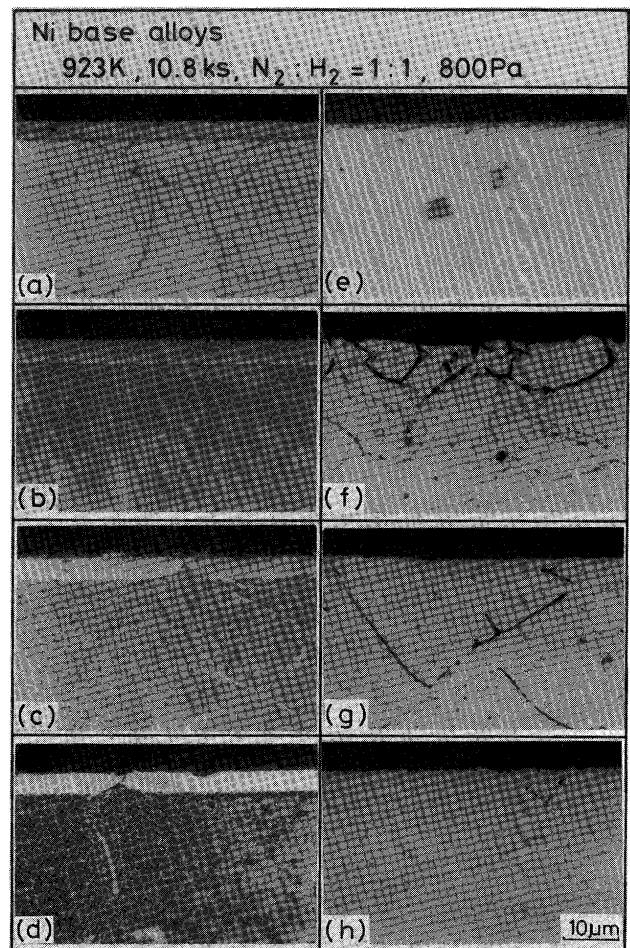


Fig. 3 Microstructure on crosssection of Ni alloys after PIN treatment at 923K for 10.8ks, electroetched by 10% oxalic acid solution; (a) Inconel 600, (b) Inconel 625, (c) Inconel 713C, (d) Udimet 500, (e) Hastelloy B, (f) Permalloy, (g) Monel, (h) pure Ni

for each alloys and pure Ni at nitriding temperature 923K and nitriding time 10.8ks by electroetching using 10% oxalic acid solution.

Obvious nitrided layer was not observed in pure Ni, Monel and Permalloy which showed no remarkable surface hardening, though in case of Permalloy grain boundary became appeared by etching only near the surface region.

On the contrary, nitrided layer was clearly observed in Inconel 600, 625, 713C, Udimet 500 and Hastelloy B which showed remarkable surface hardening. There were two types of nitrided layer, one is a single layer as Inconel 600, Udimet 500 and Hastelloy B as shown in Fig. 3 (a), (d) and (e), and the another is two layers as Inconel 625 and 713C as shown in Fig. 3 (b) and (c). Nitrided layer thickness was 3, 5, 3.5, 4 and 1  $\mu\text{m}$  for Inconel 600, 625, 713C, Udimet 500 and Hastelloy B, respectively.

In additions, there were inclusions which seemed to be MC type in base metal of Inconel 713C and Udimet 500 as shown in Fig. 3 (c) and (d) and these inclusions prevented to form the nitrided layer beneath them<sup>7)</sup>. Therefore, it was considered that these inclusions act as the barrier to the diffusion of nitrogen from specimen surface into interior of it.

### 3.3 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 by means of EPMA. Figure 4 (a) and (b) show the typical results of EPMA analysis for Inconel 625 and Udimet 500 after nitriding at 923K for 10.8ks, respectively. Copper was electrolytically plated on the surface of specimen after PIN treatment to protect the detail of specimen surface.

It was made clear that nitrogen concentrated only in the nitrided layer and there was no difference in the contents of Ni and alloying elements such as Cr, Mo, Nb, Ti, Al and so on between the nitrided layer and base metal. This means that nitrided layer is not composed only of the dense nitride itself, but it is formed as the nitride precipitated layer which is considered as follows; (i) nitrogen diffused into the interior of alloy from its surface, (ii) nitrogen combined with alloying element there, and (iii) nitrides precipitated in a nitrogenous matrix of alloy.

Same distributions of nitrogen and alloying elements were observed in the nitrided layer of another alloys. On the contrary, only slight concentration of nitrogen near the surface of specimen was observed in Permalloy. In pure Ni and Monel, however, nitrogen was not detected in a crossection of treated specimen.

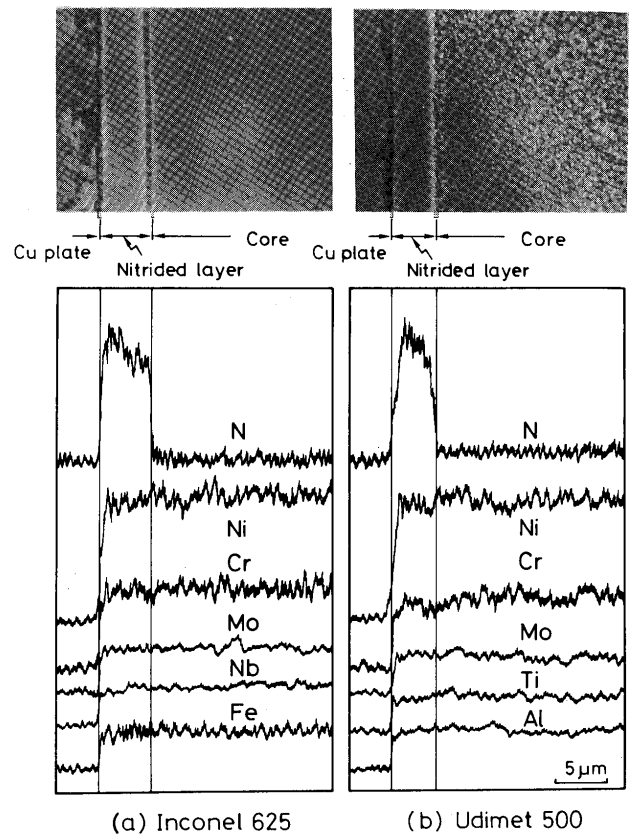


Fig. 4 EPMA analysis on crosssection after PIN treatment at 923K for 10.8ks, (a) Inconel 625, (b) Udimet 500

### 3.4 Effect of nitriding time and nitriding temperature on thickness of nitrided layer

Figure 5 shows that the relation between a square of the thickness of nitrided layer and nitriding time at a constant nitriding temperature 923K for Inconel 600, 625, 713C, Udimet 500 and Hastelloy B which showed the obvious nitrided layer.

A linear relationship was obtained between the square of the thickness of nitrided layer and nitriding time for more than 3.6ks for each alloy. This means that the formation of the nitrided layer follows the parabolic law due to the diffusion of nitrogen in Ni alloys. That is to say, the following relation is represented;

$X^2 = kt$ , where  $X$  is thickness of nitrided layer,  $k$  is growth rate coefficient of the nitrided layer and  $t$  is nitriding time. From the results of Fig. 5,  $k$  for each alloy was measured as followed, 0.71, 1.52, 0.95, 1.37 and 0.2 ( $\times 10^{-3} \mu\text{m}^2/\text{s}$ ) for Inconel 600, 625, 713C, Udimet 500 and Hastelloy B, respectively. Therefore, as to the effect of alloying element on the growth rate of nitrided layer, it is considered that chromium is much more effective than molybdenum, and in addition, multiplicative effect of other minor alloying elements such as Ti, Nb, Ta,

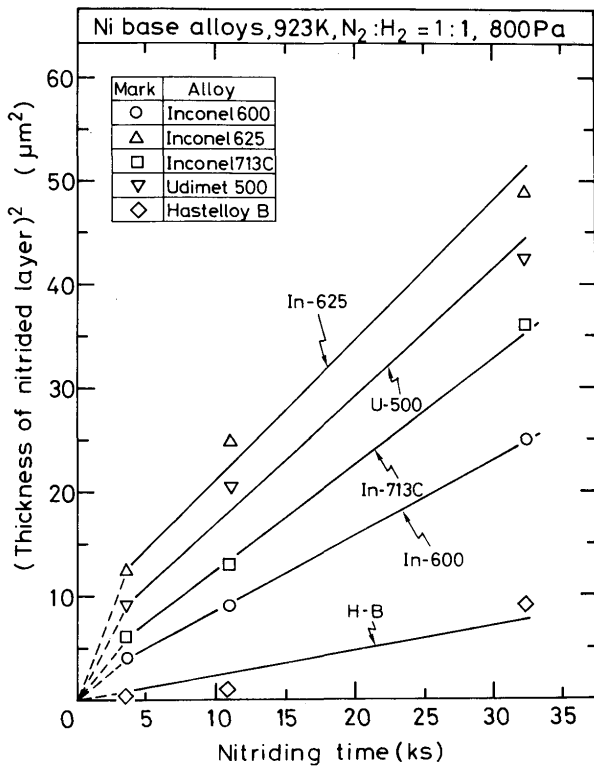


Fig. 5 Relation between square of thickness of nitrated layer and nitrating time for Ni alloys

As so on is also suggested.

The growth rate of nitrated layer at nitrating time less than 3.6ks was higher than that at more than 3.6ks for each alloy. A same phenomenon was observed in carbon steels and stainless steels by PIN treatment<sup>8)</sup>. It is considered that at the first stage of PIN treatment the thin nitrated layer deposits on the specimen surface, and then nitrogen diffuses into the specimen through this thin nitrated layer.

The effect of nitrating temperature on the thickness of nitrated layer is shown in Fig. 6 at nitrating time 10.8ks. Thickness of nitrated layer increased rapidly with the increase in nitrating temperature, and chromium-contained alloys such as Inconel 625 and Udimet 500 showed thicker nitrated layer and molybdenum-contained alloy, Hastelloy B was the thinnest nitrated layer. From the results of Figs. 5 and 6, activation energy for the formation of nitrated layer by PIN treatment was estimated for each alloy, as followed; 38.7, 41.5, 44.3, 35.9 and 94.5 (kJ/mol) for Inconel 600, 625, 713C, Udimet 500 and Hastelloy B, respectively. These values may consider as the activation energy of the nitrogen diffusion into each Ni alloy.

However, unfortunately, within the author's knowledge, the diffusion characteristics of nitrogen in Ni alloys have not been reported. In another alloys, for example, the activation energy for the formation on nitrated layer

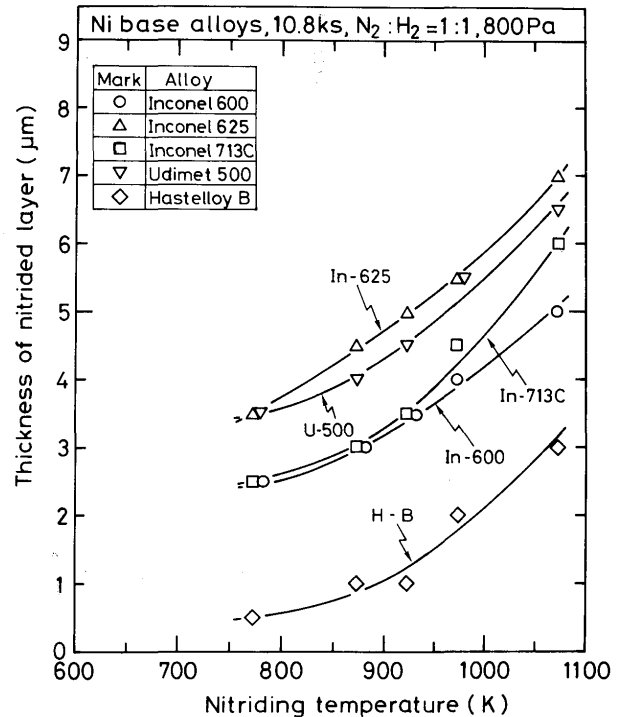


Fig. 6 Relation between thickness of nitrated layer and nitrating temperature for Ni alloys

in carbon steel and stainless steel by PIN process were 80-120(kJ/mol)<sup>8-10)</sup>.

### 3.5 X-ray diffraction analysis

Figure 7 (a) to (d) shows the result of X-ray diffraction analysis for the surface of specimens of Permalloy, Hastelloy B, Inconel 600 and 625, respectively after the treatment at 923K for 10.8ks, and (e) shows an example of X-ray diffraction pattern at higher nitrating temperature, 1073K for 10.8ks for Inconel 625.

As a result, there were three types of diffraction peaks in these analyses. One type of diffraction pattern shown as 'γ' in Fig. 7 was from base metal beneath the nitrated layer and these peaks were very sharp in all alloys. The second type of diffraction peaks were from the nitride of alloying element, such as Fe<sub>2-3</sub>N, MoN and Mo<sub>2</sub>N and CrN for Permalloy, Hastelloy B and Inconel 600 and 625, respectively. Diffraction peaks of CrN in Inconel 625 was slightly shifted to lower diffraction angle than those stoichiometric CrN. It seemed that the lattice parameter of CrN was changed due to that a part of chromium in CrN was substituted by another alloying elements such as Mo, Nb.

Moreover, the third of diffraction peaks shown as 'M' in Fig. 7 were observed near each peak of base metal, γ. Therefore, it was considered that M phase has the same crystal structure as the base metal of each alloy, though it was not detected in ASTM Powder Diffraction Files. In

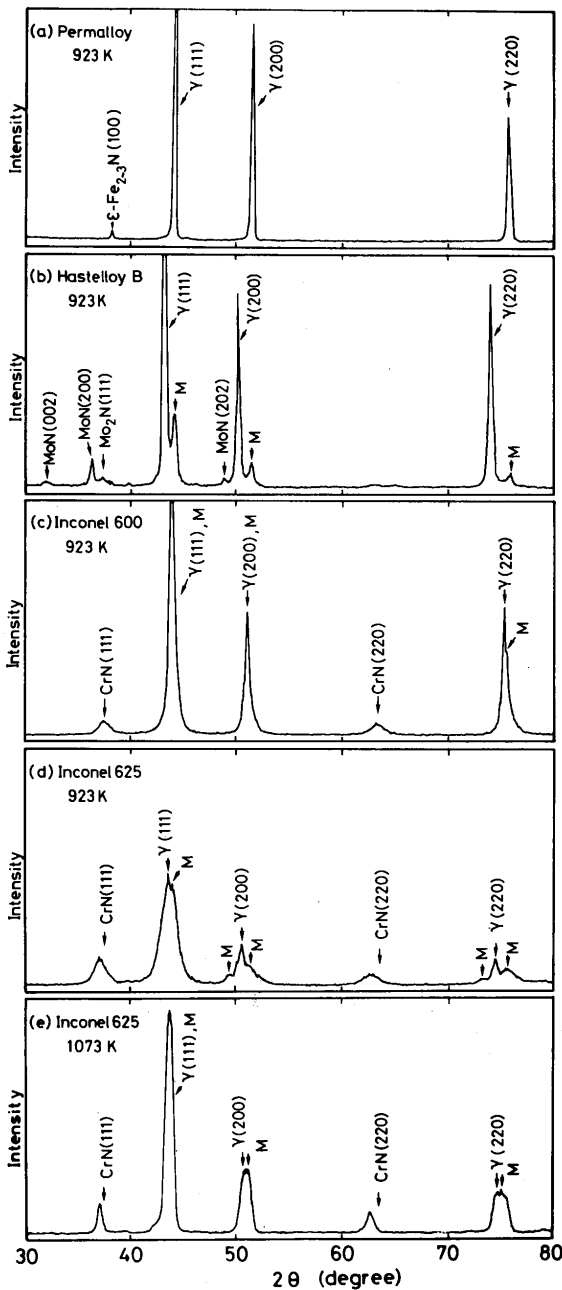


Fig. 7 X-ray diffraction pattern of surface of specimens after PIN treatment, (a) Permalloy, (b) Hastelloy B, (c) Inconel 600, (d) Inconel 625, (e) Inconel 625 (1073K)

addition, M phase was observed only in the alloys showing the obvious nitrided layer and not observed in alloys with no nitrided layer. Judging from the results of EPMA and X-ray diffraction analyses, it is considered that M phase is a matrix of nitrided layer in which fine nitrides precipitate.

Another attention should pay to the broadening of diffraction peaks of nitride and M phase. The widths of diffraction peaks of both nitrided layer and M phase (matrix of nitrided layer) were much different with

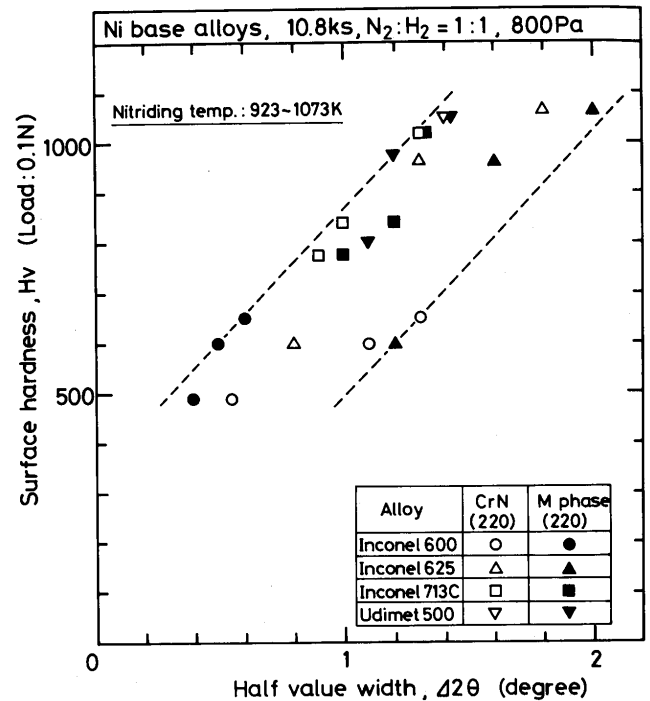


Fig. 8 Relation between surface hardness and half value width of X-ray diffraction pattern of nitrides and matrix of nitrided layer

alloy type and treating temperature, and it seemed that the broadening of diffraction peaks of nitride and matrix of nitrided layer were concerned with surface hardening.

In order to confirm it, the surface hardness of chromium-contained alloys is shown in Fig. 8 as a functions of the half value width of diffraction peaks of nitride and matrix of nitrided layer. Open and solid marks in Fig. 8 show the half value width of diffraction peaks of nitride CrN(220) and the matrix of nitrided layer M(220) corresponding to the base metal  $\gamma$ (220), respectively.

As a result, there is an approximate relationship between the half value width of these peaks and the surface hardness, which is linearly increased with the half value width of nitrided and matrix of nitrided layer, though some scattering in data is observed. The broadening of diffraction peaks of nitride and matrix of nitrided layer in X-ray diffraction analysis shows that a fine nitride having the coherency with the matrix was precipitated and caused ununiform microstrain in the matrix of nitrided layer around precipitated nitride<sup>11)</sup>. It is considered that the surface hardening of Ni alloys by PIN treatment was due mainly to ununiform microstrain in the matrix of nitrided layer caused by dispersive precipitations of fine nitride, and hardness decrease at higher temperature was owing to the decrease of this microstrain caused by the coarsening of nitride.

#### 4. Conclusions

The probability of surface hardening of Ni alloy by means of Plasma Ion Nitriding (PIN) process was investigated for pure Ni and various commercially-used Ni alloys, such as Inconel 600, 625, 713C, Udimet 500, Hastelloy B, Permalloy and Monel. As a result, the following conclusions were obtained;

- (1) Alloys containing some nitride forming elements, such as Inconel 600, 625, 713C, Udimet 500, Hastelloy B and Permalloy were possible to be hardened by means of PIN process, but Monel and pure Ni with no nitride forming element were not hardened.
- (2) Surface hardness depended on both nitriding temperature and kinds of alloy. Maximum surface hardness which was observed at 923K were Hv650, 1100, 1000, 1050 and 500 for Inconel 600, 625, 713C, Udimet 500 and Hastelloy B, respectively, but surface hardness of Permalloy was Hv230.
- (3) Nitrided layer was observed in alloys showing remarkable surface hardening as Inconel 600, 625, 713C, Udimet 500 and Hastelloy B and it was estimated by EPMA results that nitrided layer was formed as nitrided precipitated layer.
- (4) The growth rate of nitrided layer followed the parabolic law except at the early stage of nitriding up to about 3.6ks.
- (5) From the result of X-ray diffraction analysis, CrN for Inconel 600, 625, 713C and Udimet 500, MoN and Mo<sub>2</sub>N for Hastelloy B were detected as nitride together with diffraction peaks from the matrix of nitrided layer and base metal beneath it. Diffraction peaks of these nitrides and matrix of nitrided layer were very broad and the half value width of these peaks had a good relationship with surface hardness, which was linearly increased as the increase of the half value width. Therefore, it was considered that hardness increase by PIN process was due to ununiform microstrain caused by the precipitation of

such nitrides in nitrided layer.

#### Acknowledgements

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