Rapid Plasma Nitriding Process by Means of Hollow Cathode Glow Discharge†

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Abstract

The probability of rapid nitriding process assisted by hollow cathode glow discharge was examined mainly for austenitic stainless steel SUS 304.

Hollow cathode glow discharge was easily realized by arranging some specimens on a cathode plate so that the distance between each specimen coincided with an optimum value, which was different depending on gas pressure as 3 mm for 800 and 1330 Pa, 5 mm for 270 Pa and 15 mm for 80 Pa at $N_2 + H_2$ mixed gas. At these conditions, nitriding speed was increased to about 2 times as fast as that with a conventional plasma nitriding process even at the same nitriding temperature and time without any decrease in hardness of nitrided layer. This increase in nitriding speed was considered to be due to the high ionization rate of hollow cathode glow discharge in comparison with ordinary glow discharge.

KEY WORDS: (Nitriding) (Plasma Nitriding) (Hollow Cathode) (Hardness) (Surface Hardening) (Stainless Steel) (Ni Alloy) (Heat Resistant Alloy)

1. Introduction

Plasma nitriding process assisted by glow discharge has become more popular in surface hardening processes because of its excellent features such as energy and labour saving process, good reproducibility of the properties of treated layer and no requirement for anti-pollution equipment.

However, when low nitrogen diffusible materials such as austenitic steels are treated, the long time treatment is required to get a thick nitrided layer even with plasma nitriding process which shows faster growth rate of nitrided layer than other conventional nitriding processes[1].

In order to increase the growth rate of nitrided layer, the increases of treating temperature and of nitrogen partial pressure in treating atmosphere are both effective methods. However, there are limitations for each method, because high treating temperature decreases the hardness of nitrided layer and higher atmospheric pressure than about 3000 Pa makes glow discharge unstable.

As in plasma nitriding process, nitrogen transfers from atmosphere into the specimen mainly by the bombardment of nitrogen ions, it is considered that the increase of nitrogen ionization rate in plasma increases the nitrogen concentration transferred into the specimen surface and this will result in the increase in the growth rate of nitrided layer.

Magnetron-assisted glow discharge and hollow cathode glow discharge are both effective processes to increase the ionization rate in plasma. As latter method is quite simple and requires no other special equipment such as magnetron generater, hollow cathode discharge has been employed in this report to enhance the glow discharge, and the probability of increasing growth rate of nitrided layer by this method has been examined mainly for austenitic stainless steel.

2. Mechanism of hollow cathode glow discharge

In hollow cathode discharge, discharge current remarkably increases in comparison with that of ordinary glow discharge even with same discharge voltage. This reason is generally considered as follows[2]; **Figure 1** shows the schematic illustration of hollow cathode discharge between parallel cathode plates set to overlap each negative glow region. At the ordinary glow discharge with a single cathode, fast electron emitted from the cathode surface escapes away through a negative glow region to an anode. Therefore the probability of electron-neutral gas atom collision is low. On the contrary, in hollow cathode discharge, fast electron emitted from cathode (1) in Fig. 1 run into the opposite dark space in front of cathode (2) through a negative glow region and decrease its speed there, but after then it is again accelerated toward the opposite cathode (1). Thus as electron repeats this return movement between two cathodes until its kinetic energy decreases enough for electron to be drawn out toward the

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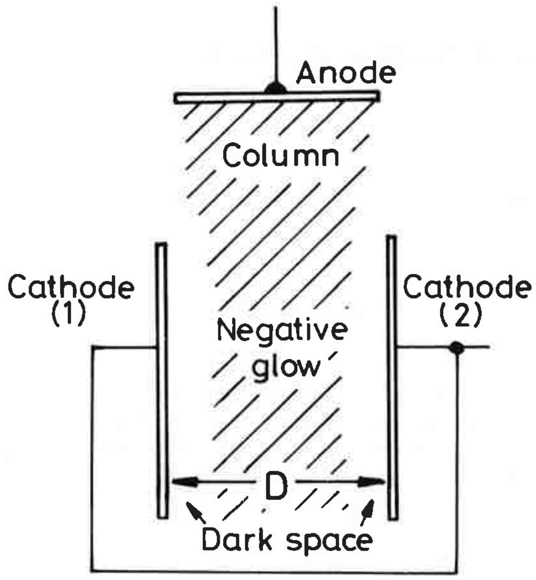

Fig. 1 Schematic illustration of a hollow cathode between two parallel cathode plates

Table 1 Chemical compositions of materials used

Alloys	Chemical compositions (wt%)										
	C	Mn	Si	Cr	Ni	Co	Mo	Nb+Ta	Fe	Ti	Al
SUS 304	0.07	0.91	0.52	18.12	8.74	-	-	-	Bal.	-	-
SUS 430	0.06	0.52	0.61	16.54	0.13	-	-	-	Bal.	-	-
Inconel 625	0.02	0.20	0.40	21.60	Bal.	-	8.3	3.7	2.6	0.2	0.1
Udimet 500	0.09	-	-	18.80	Bal.	16.7	3.5	-	0.2	3.2	3.0

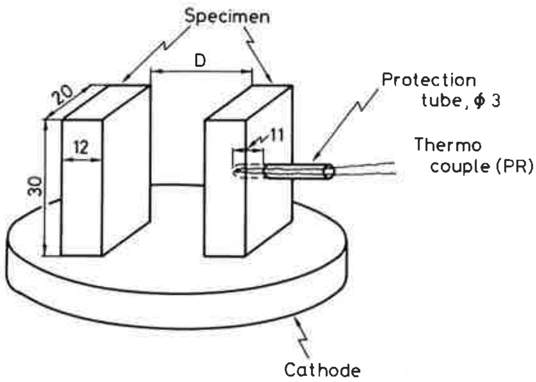

Fig. 2 Specimen arrangement on an cathode plate

anode, the probability of electron-neutral atom collision much increases. Hence this results in the increase of the degree of ionization and of discharge current in hollow cathode discharge.

The purpose of this study is to discuss that the increase in the degree of ionization may result in the increase in the growth rate of nitrided layer at plasma nitriding process.

3. Materials Used and Plasma Nitriding Apparatus

3.1 Materials used

Mainly austenitic stainless steel SUS 304 and partly ferritic stainless steel SUS 430, Ni base alloys Inconel 625 and Udimet 500 were used as specimens for plasma nitriding treatment. The chemical compositions are shown in **Table 1**.

3.2 Plasma nitriding apparatus

A conventional plasma nitriding apparatus[3)] by a dc glow discharge between a vacuum chamber wall as an anode and nitriding specimen as a cathode was used for treatment.

Hollow cathode glow discharge was briefly realized by placing two specimens ($30^l \times 20^w \times 12$ mm^t) parallel for each other on a stainless steel cathode plate of 60 mm in diameter as shown in **Fig. 2**, when the distance between each specimen was an optimum value, D_{op}. Therefore in order to find out this D_{op}, the specimen distance, D was varied from 1 to 50 mm for the various gas pressures of 80 to 1330 Pa.

In order to maintain the temperature of inner surfaces of specimens subjected to hollow cathode discharge to a constant value, the temperature near inner surface was measured by 0.3 mm dia. PR thermocouple protected with 3 mm dia. alumina tube which was inserted from outer surface of a specimen to about 1 mm beneath the inner surface as shown in Fig. 2.

Specimen surface was ground with emery paper #1200 and degreased with acetone.

After the chamber was evacuated to 0.65 Pa, nitrogen and hydrogen mixed gas ($N_2 : H_2 = 1 : 1$) was introduced into the chamber and dc glow discharge was generated under a constant gas pressure. Nitriding temperature measured by the above method was kept to 793 K and 823 K for stainless steels and Ni base alloys, respectively for 3.6 to 21.6 ks of treating time, and gas pressure was also varied from 80 to 1330 Pa.

After treatment, hardness profile on a crosssection of the specimen and nitrided layer thickness were measured to make clear the hollow cathode effect to these factors.

4. Results and Discussions

4.1 Discharge characteristics

Figure 3 (a), (b) and **(c)** show typical scenes of glow discharge in $N_2 + H_2$ mixed gas at 800 Pa on a single specimen and double specimen of 3 mm and 30 mm of specimen distances, D respectively, at 793 K of specimen temperature, where dark space surrounding cathode specimen surface and also negative glow region illuminating at outer region of the dark space are clearly seen.

Intense illumination occurred between specimens at D = 3 mm, which was the most typical feature of hollow cathode discharge, but such illumination was weakened at

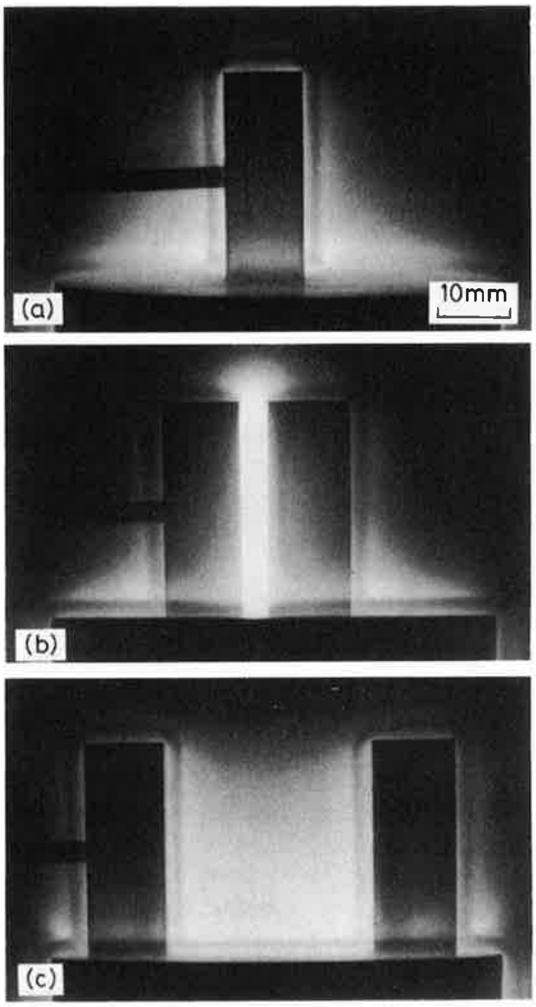

Fig. 3 Typical scenes of glow discharge in $N_2 + H_2$ mixed gas at 800 Pa; (a) single specimen, (b) D = 3 mm, (c) D = 30 mm

D = 30 mm, though it was even stronger than that in negative glow region of ordinary glow discharge with single cathode.

Figure 4 shows the variations of discharge voltage and current, electric power input against the specimen distance, D as an open mark in the figure for various gas pressure of 270, 800 and 1330 Pa with $N_2 + H_2$ mixed gas. Those values for single specimen was also shown as solid mark, which was regard as D = 0 mm, for comparison. The specimen temperature was kept constant at 793 K by controlling electric power input.

The minimum in each parameter was appeared at the same D value, but which was different depending on gas pressure, that is, about 5 mm for 270 Pa and 3 mm for 800 and 1330 Pa. In these cases, intense illumination as shown in Fig. 3 (b) occurred.

In less D value, discharge voltage increased abruptly and became to the obstructed glow discharge condition. In larger D value, all parameters were increased as the increase in D value and became to satulate at more than 30 mm in D for 800 and 1330 Pa, but didn't satulate even at 50 mm for 270 Pa.

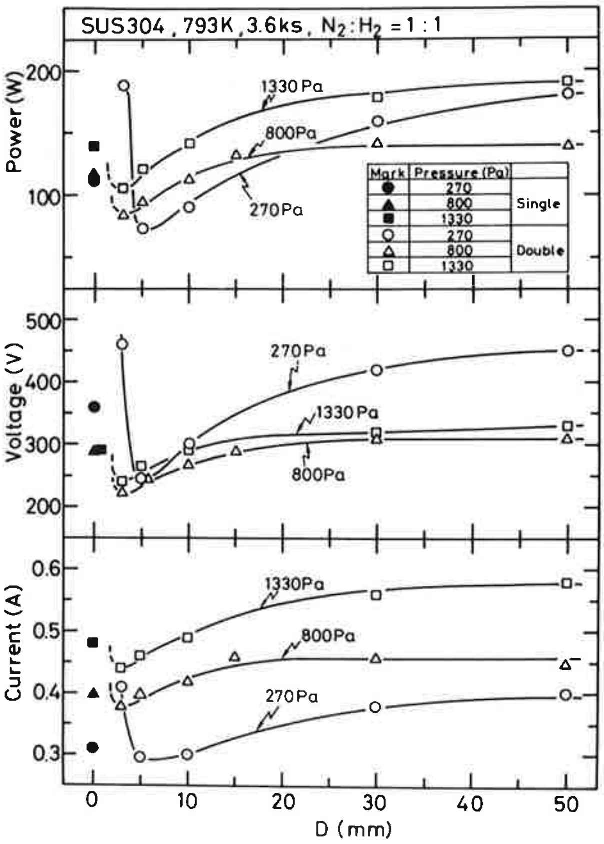

Fig. 4 Electric power input, discharge voltage and current vs. specimen distance, D at various gas pressure

In general, when hollow cathode discharge occurs, discharge current is much increased even at a constant voltage and this results in the increase in specimen temperature. However, as in Fig. 4 specimen temperature was kept constant, these parameters was decreased when hollow cathode discharge was appeared.

Therefore according to the results drawn from Figs. 3 and 4, the D value showing the minimum in discharge parameters for each gas pressure is regarded as the optimum D value to realize hollow cathode discharge for each gas pressure.

4.2 Hardness of nitrided layer

Figure 5 shows typical hardness distributions on cross-section of nitrided specimens at 793 K for 3.6 ks in $N_2 + H_2$ mixed gas at 800 Pa for various D values.

Sharp increase in hardness near specimen surface in comparison with base metal hardness, Hv 200 was observed for each specimens. Hardness was almost uniform through nitrided layer, Hv 1200 to 1300 independent of D value. These increase in hardness is due mainly to the precipitation of CrN according to the X-ray diffraction analysis.

However, hardened zone width was much different with D values. Maximum width of hardened zone appeared at D = 3 mm, which just coincided with hollow cathode discharge. The increase in D value decreased the hardened zone width, but which was wider than that of single specimen even at D = 50 mm.

From these results it is considered that when hollow cathode discharge was utilized for plasma nitriding, much wider hardened layer can be obtained at the same treating temperature and time and moreover much less electric power input.

4.3 Thickness of nitrided layer

Figure 6 (a) to (f) shows typical crosssectional microstructures of nitrided specimens near surface for single specimen and double specimen of D = 1, 3, 10, 30 and 50 mm, respectively at the same nitriding conditions for Fig. 5.

Gray layer with smooth interface between base metal is a nitrided layer, which just coincided with the hardened zone revealed in Fig. 5.

Figure 7 shows the relation between nitrided layer thickness and D value for the various gas pressure from 80 to 1330 Pa in comparison with the case of single specimen under the same nitriding conditions of 793 K × 3.6 ks, though discharge voltage and current were changed depending on gas pressure and D value as mentioned in Fig. 4.

Mostly nitrided layer thickness in double specimen was wider than that in single specimen, though in D = 1 mm for 800 and 1330 Pa, 3 mm for 270 Pa and less than 10 mm for 80 Pa, no clear nitrided layer was formed as shown, for example, in Fig. 6 (b) for 800 Pa because of the occurrence of obstructed glow discharge.

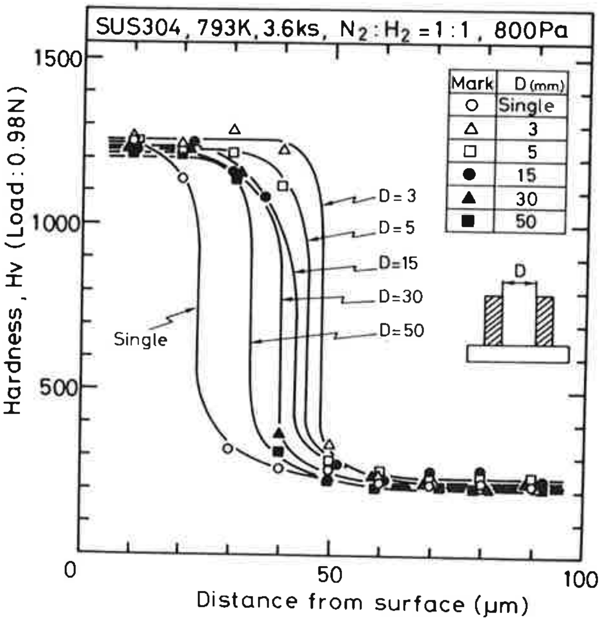

Fig. 5 Hardness distributions on crosssections of nitrided SUS 304 specimen at 793 K for 3.6 ks in N_2 + H_2 mixed gas at 800 Pa for various D values

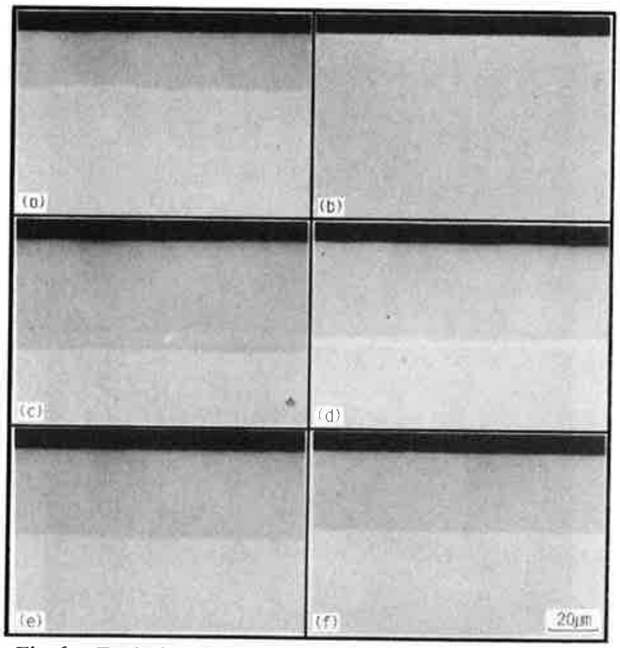

Fig. 6 Typical crosssectional microstructures of nitrided SUS 304 specimens at the same conditions as Fig. 5, (a) single specimen, (b) D = 1 mm, (c) D = 3 mm, (d) D = 10 mm, (e) D = 30 mm, (f) D = 50 mm

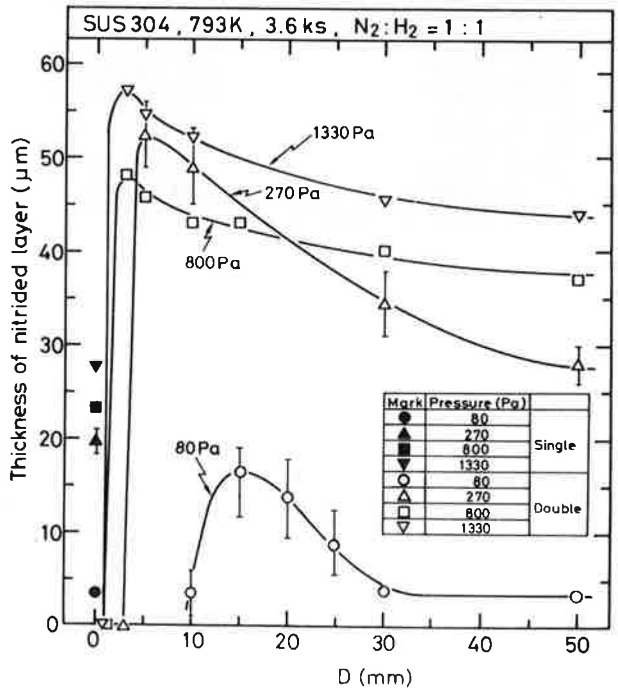

Fig. 7 Relation between nitrided layer thickness and D value for various gas pressure for 80 to 1330 Pa

There is an optimum D value (D_{op}) to get a maximum thickness for each gas pressure, and D_{op} decreased as the increase in gas pressure as 3 mm for 800 and 1330 Pa, 5 mm for 270 Pa and 15 mm for 80 Pa. At these D_{op} value, abrupt decrease in discharge voltage and current and in addition a intense illumination were also observed. Therefore these phenomena means the occurrence of hollow cathode discharge at these D_{op} values for each gas pressure.

Increasing D value more than D_{op} gradually decreased the nitrided layer thickness to almost the same thickness at single specimen for each gas pressure.

The reason of presence of the optimum value in D is considered as follows; in order to realize hollow cathode discharge in parallel double specimen, it is necessary to overlap the each negative glow region effectively.

However, very narrow specimen distance causes the obstructed glow discharge impossible for nitriding, and on the contrary increasing specimen distance decreases the overlapped region in each negative glow region and this decreases the hollow cathode effect.

As to the thickness of nitrided layer, gas pressure also affected the thickness, which was increased as the increase in gas pressure as shown in Fig. 7 for single and double specimens. However, at 270 Pa in D = 5 and 10 mm nitrided layer was exceptionally thicker than the maximum thickness at 800 Pa. Generally ionization rate in hollow cathode discharge is larger at low pressure because of a wide negative glow region which enables an effective overlap of each negative glow region. Much lower gas pressure as 80 Pa, however, even with high efficiency of ionization, the number of ions is not so increased because of low density of neutral gas atoms to be ionized.

Therefore in order to utilize this hollow cathode effect to increase the thickness of nitrided layer, more than about 270 Pa for an gas pressure of $N_2 + H_2$ mixed gas is recommended.

Nextly, according to the test results the D_{op} value for various gas pressure can be estimated by cathode dark space for each gas pressure. **Figure 8** shows the variations of cathode dark space and D_{op} value against total gas pressure. As well known, cathode dark space was decreased as the increase in gas pressure, and the same relationship was observed between D_{op} and gas pressure. From this figure it was made clear that D_{op} was 2 to 3 times as wide as cathode dark space.

4.4 Application of hollow cathode method to various materials

Figure 9 shows the comparison of thickness of nitrided layers treated with conventional plasma nitriding process with single specimen and hollow cathode process with double specimen at the optimum D value, 3 mm for 800 Pa for austenitic SUS 304 and ferritic SUS 430 stainless steels at 793 K for 3.6 ks and Ni base heat resistant alloys Inconel 625 and Udimet 500 at 873 K for 10.8 ks.

Thickness of nitrided layer by hollow cathode process was about twice those by conventional process for all materials used under the same nitriding temperature and time.

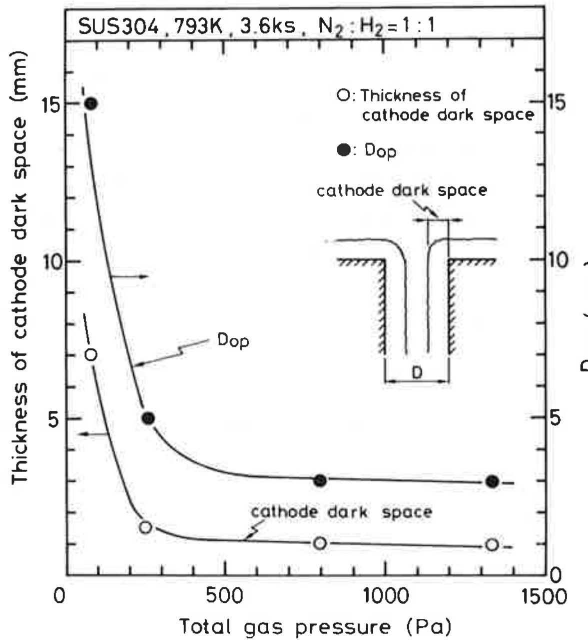

Fig. 8 Variation of cathode dark space and the optimum specimen distance, D_{op} against gas pressure

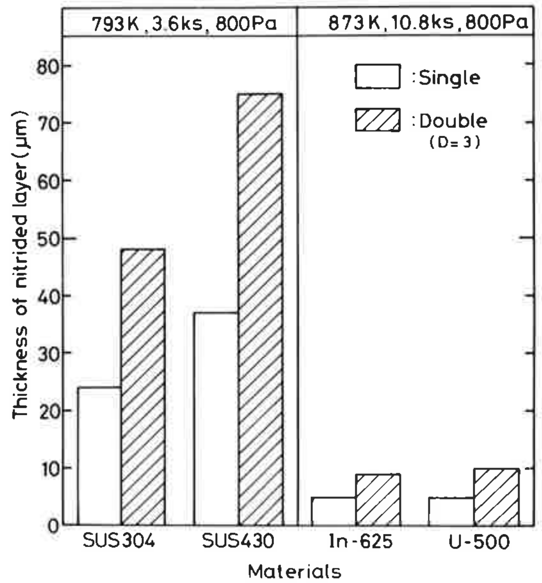

Fig. 9 Comparison of nitrided layer thickness with conventional and hollow cathode plasma nitriding processes (D = 3 mm, 800 Pa) for SUS 304, SUS 430 and Ni base heat resistant alloys Inconel 625 and Udimet 500

5. Conclusions

The effect of hollow cathode process by using a parallel double cathode specimen on the thickness of nitrided layer has been examined by changing the distance between two parallel specimens at various nitriding gas pressure mainly for austenitic SUS 304 stainless steel.

Main conclusive remarks obtained are as follows;

(1) Hollow cathode process enabled to increase the nitriding speed about 2 times as fast as that with conventional plasma nitriding process without any decrease in hardness of nitrided layer and in addition without any other special equipment.
(2) There is, however, an optimum distance (D_{op}) between each specimen placed on an cathode depending on gas pressure in order to increase the nitriding speed, that is, 3 mm for 800 and 1330 Pa, 5 mm for 270 Pa and 15 mm for 80 Pa, which were almost twice to third that of cathode dark space for each gas pressure.
(3) At the optimum specimen distance, D_{op}, discharge voltage and current required to keep the specimen temperature were much decreased in comparison with that of conventional plasma nitriding process because of hollow cathode effect.

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