Ion Nitriding Hardening of Non Ferrous Alloys (Report I)†

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Abstract

A new ion nitriding apparatus (grow discharge ionized process) was installed and with this process nitriding surface hardening has been tried for various commercial nonferrous and some ferrous metals and alloys. As a result, the selection of the metals and alloys which can be done surface hardening with nitriding process was tentatively established.

KEY WORDS: (Ion Nitriding) (Nitriding) (Hard Surfacing) (Nonferrous Metal) (Stainless Steel) (Heat Resistant Alloy) (Refractory Alloy) (Reactive Alloy) (Glow Discharge)

1. Introduction

For the purposes of improvement for metal surface against abrasion, injury, cavitation, corrosion and so on, various surface hardening processes have been developed and investigated so far.

Nitriding of metal surface with ionized nitrogen gas (glow discharge ionized nitriding process) is one of these processes[1-6].

Nitriding surface treatment of low and medium carbon and low alloy steels has been widely investigated so far and already some of them are used for industrial purposes. While within the authors' knowledge there are few investigations for surface hardening of nonferrous metals and alloys by nitriding processes especially by ion nitriding process[7-9]. Therefore, as a preliminary investigation the authors have investigated here for the surface hardening of nonferrous metals and alloys in the main and ferrous in a part by means of nitriding process. All-inclusive results for the ion nitriding process of the metals and alloys were reported after a short introduction of the apparatus installed.

2. Experimental Procedure

2.1 Ion nitriding process used

Figure 1 shows the illustration of principle for ion nitriding process used in this experiment. The test specimen which is nitrified is set in a chamber. The chamber is firstly evacuated to less than 10^{-3} Torr by mechanical and oil diffusion pumps and filled to several Torr with N_2 gas with or without H_2 gas. Consequently keeping the gas atmosphere glow discharging, specimen negative, is continued for several hours under a constant elevated temperature. By a control of discharge voltage temperature of the specimen is kept at a constant through an optical pyrometer. **Figure 2** shows overall view of the apparatus of ion nitriding process used.

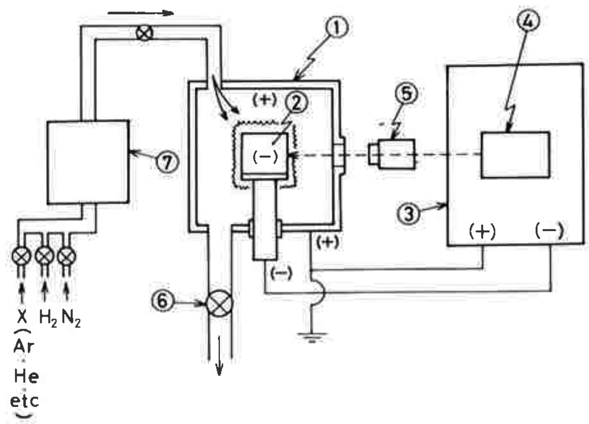

Fig. 1 Schematic illustration of principle for ion nitriding process used in this experiment

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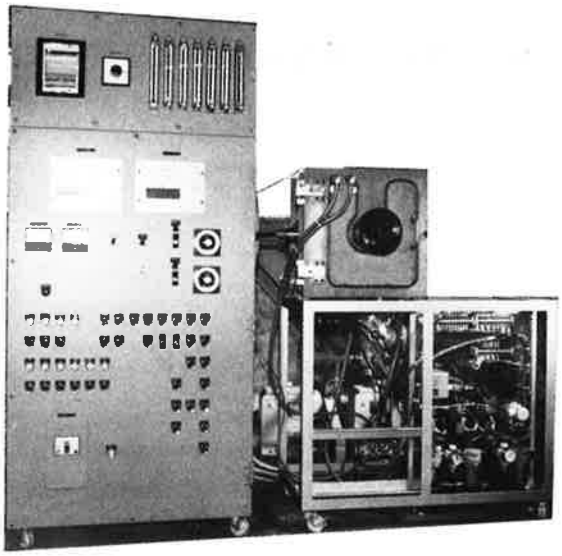

Fig. 2 Overall view of the apparatus of ion nitriding process used.

2.2 Materials and treatment conditions used

Materials which were treated with ion nitriding process in this experiment are reactive and refractory metals of IVa, Va and VIa families in periodic table, nickel and iron-nickel alloys, stainless steels, heat-resistant alloys, copper and copper alloys and aluminum and aluminum alloys which are commercially used. The specimen nitrified for these materials was a square sheet in 10 mm in width and 2 to 3 mm in thickness, and the surface was polished with sand paper of #1500 and cleaned with acetone reagent in advance.

Table 1 shows the condition of nitriding treatment for each metal and alloy as treatment temperature x hours x atmospheric pressure x mixing ratio of atmospheric gases.

Table 1 Materials used and treating condition for ion nitriding process

Material	Ion-nitriding condition (°C)×(hrs)×(Torr)×(Gas $N_2:H_2$)
Reactive & refractory metals	900 × 1 × 6 × Pure N_2
Heat resistant alloys	900 × 1 × 6 × Pure N_2 700 × 3 × 6 × 1:1
Nickel & its alloys	700 × 3 × 6 × 1:1
Steels	550 × 3 × 6 × 1:1
Stainless steels	550 × 3 × 6 × 1:1
Copper & its alloys	700 × 3 × 6 × 1:1
Aluminum & its alloys	500×2/3×6 × 1:1

3. Experimental Results

3.1 Reactive and refractory metal and alloy

For this category the authors have used metals and alloys of commercial titanium (Ti), Ti-6Al-4V, Ti-8Mn, commercial zirconium (Zr) and hafnium (Hf) as IVa family, commercial vanadium (V), niobium (Nb) and tantalum (Ta) as Va and commercial chromium (Cr), molybdenum (Mo), TZM and tungsten (W) as VIa. The experimental results are collectively tabulated in **Table 2** in which probability of nitride surface hardening, treating condition, hardnesses of surface and base metal in Vickers number of 25g load and these ratio, thickness of hardened surface layer and surface color tone after treatment are expressed. The hardness increase at the specimen surface by nitriding was possible for all these metals and alloys except W. The hardenable ratio depended on material as shown in Table 2 but it will be varied changing of treat-

Table 2 Surface hardness, thickness of hardened layer and surface color tone after ion nitriding treatment for reactive and refractory metals

Material		Surface hardening*	Treatment (°C)×(hrs)×(Torr)×(Gas)	Hardness (Hv)			Hardened zone (μ)**	Color after treatment+
				Surface** (Hvs)	Base (HvB)	Ratio (Hvs/HvB)		
Reactive & refractory metal	Ti	O	900 × 1 × 6 × (Pure N_2)	850	190	4.5	20	G
	Ti6Al4V	O		860	330	2.6	≦20	G
(IVa)	Ti8Mn	O		980	450	2.2	≦20	G
	Zr	O		650	140	4.6	60	LBB
	Hf	O		840	380	2.2	60	LG
(Va)	V	O		600	260	2.3	200	LG
	Nb	O		180	90	2.0	50	LG
	Ta	O		210	150	1.4	20	LG
(VIa)	Cr	O		650	140	4.6	20	SW
	Mo	O		1020	280	3.6	10	SW
	TZM	O		1200	310	3.9	10	SW
	W	X		530	510	1.0	-	SW
(Mother alloy)	Fe40Ti	X	900 × 1 × 6 × (Pure N_2)	600	680	<1	-	LG
	Fe70Ti	X		400	590	<1	-	G
	Fe80Zr	O		1900	590	3.2	30	SW

* O Yes, X No ** Approximate value
\+ G:Gold, LG:Light gold, LBB:Light blue-brown, SW:Silver white

ment condition. Moreover hardness increase of W will be also possible by an increase of treat temperature.

Figures 3, **4** and **5** show the hardness distributions in cross-section of material for IVa, Va and VIa families after nitriding, respectively. The most thick hardened layer was obtained in vanadium metal.

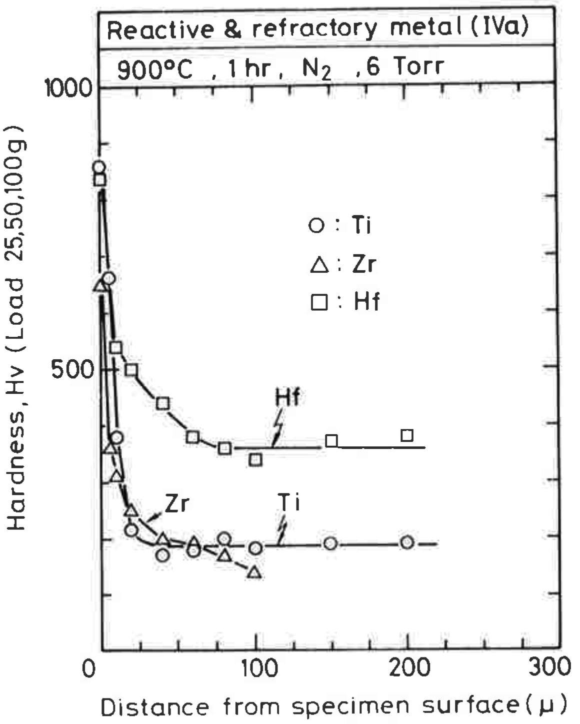

Fig. 3 Hardness distribution in cross-section of material for IVa family after nitriding.

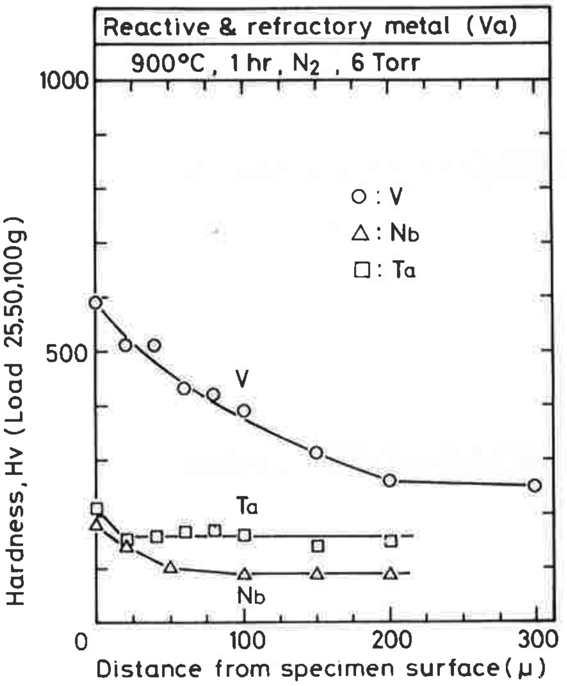

Fig. 4 Hardness distribution in cross-section of material for Va family after nitriding

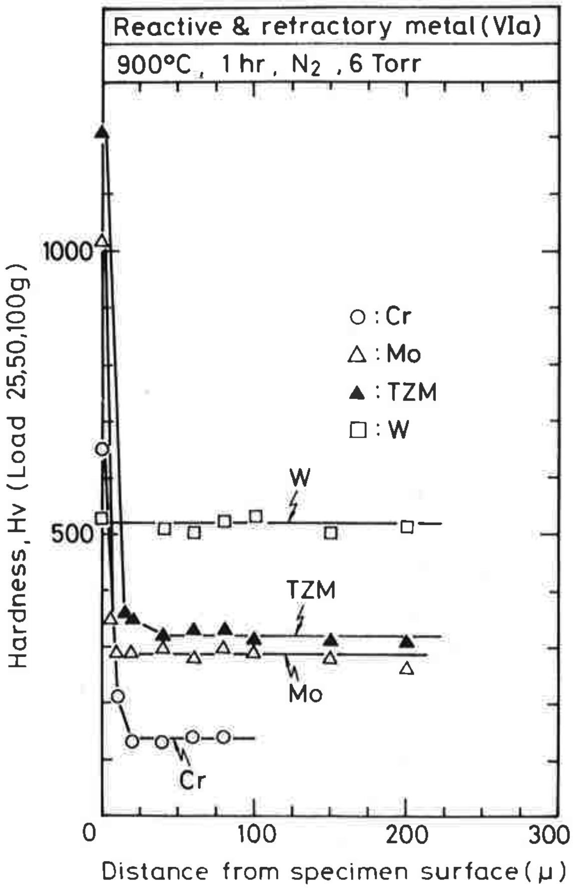

Fig. 5 Hardness distribution in cross-section of material for VIa family after nitriding

3.2 Nickel, iron-nickel alloy and stainless steel

Commercial pure iron, 9% nickel steel, 36% nickel invar alloy, commercial pure nickel and SUS 310S, 304, 316, 321, 347 and 430 stainless steels were used in this category. The results were shown in **Table 3**. As shown in Table 3 nickel metal did not show hardenability after treatment but the other metals and alloys did. Especially in stainless steels the obvious surface hardening occurred.

Figure 6 shows the hardness distributions of stainless steels. The hardness of hardened layer for SUS 321 and 347 steels shows a constant for whole layer, while that for 304, 310S, 316 and 430 shows a gradual decrease inwardly. **Figure 7(a)**, **(b)**, **(c)** and **(d)** shows the microstructures in cross-sections of SUS 310S, 304, 321 and 430 steels, respectively, after nitriding. Ferritic 430 steel shows the thickest nitride layer and high Cr-contained austenitic 310S shows the thinest layer.

Table 3 Surface hardness, thickness of hardened layer and surface color tone after ion nitriding treatment for nickel, iron-nickel alloys and stainless steels

Material		Surface hardening*	Treatment (°C)×(hrs)×(Torr)×(Gas)	Hardness (Hv)			Hardened Zone (μ)**	Color after treatment+
				Surface** (Hv_S)	Base (Hv_B)	Ratio (Hv_S/Hv_B)		
Ferro & nickel alloy	Fe	O	550×3×6×(N_2:H_2=1:1)	280	170	1.6	20	LGr
	Fe9Ni	O		480	310	1.5	10	Gr
	Fe36Ni	O	700×3×6×(N_2:H_2=1:1)	290	160	1.8	20	Bl
	Ni	X		60	55	-	-	Bl
Stainless steel	304	O	550×3×6×(N_2:H_2=1:1)	1300	210	6.2	95	LGr
	310S	O		1310	190	6.9	50	LGr
	316	O		1050	200	5.3	55	LGr
	321	O		1300	230	5.7	95	Gr
	347	O		1100	240	4.6	90	Gr
	430	O		1170	160	7.3	115	Gr

* O Yes, X No ** Approximate value
\+ LGr: Light gray, Gr: Gray, Bl: Black

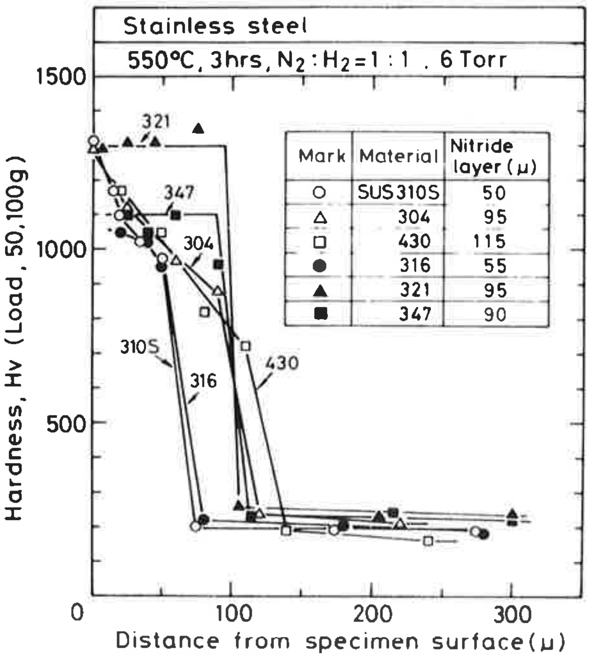

Fig. 6 Hardness distribution in cross-section of material for stainless steels after nitriding

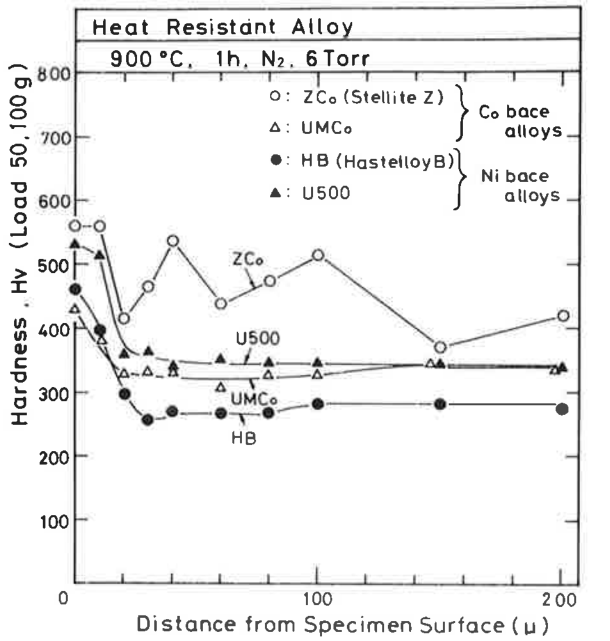

Fig. 8 Hardness distribution in cross-section of material for cobalt- and nickel-base heat resistant alloys

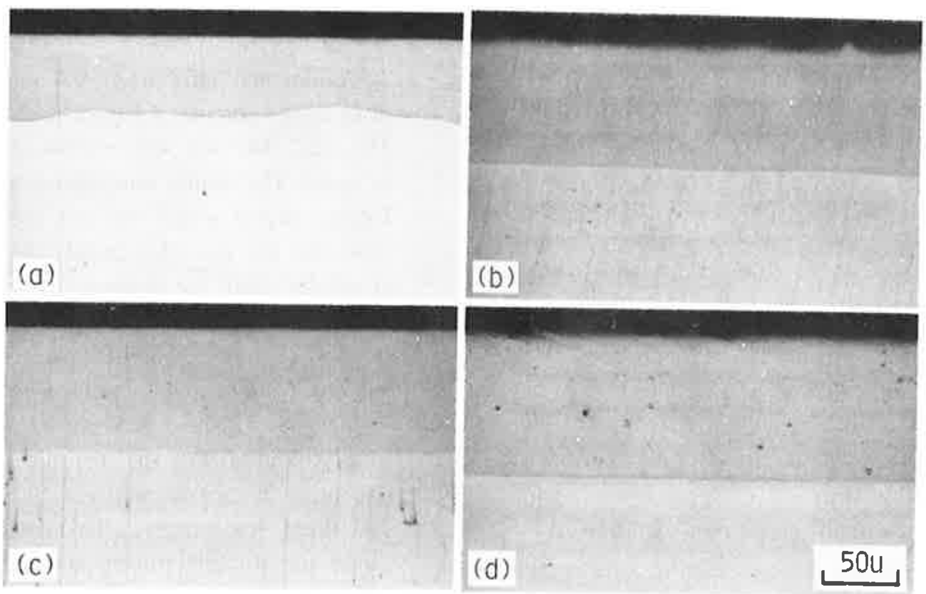

Fig. 7 Microstructure in cross-section of material for stainless steels after nitriding; (a) 310S (b) 304 (c) 321 and (d) 430

3.3 Heat resistant alloys

Iron-, nickel- and cobalt-base heat resistant alloys were included in this category. The authors have used three for iron-base, six for nickel-base and two alloys for cobalt-base. The collective results were shown in **Table 4**. The nitriding hardening for these alloys were also possible except ZCo whose hardening was not cleared. Moreover cross-section hardness distributions were shown in **Fig. 8** for cobalt- and nickel-base alloys and in **Fig. 9** for ferrous- and nickel-base alloys. **Figure 10(a), (b)** and **(c)** shows the crosssectional microstructures of nitrided specimens of Incoloy 800, Inconel 600 and UMCo.

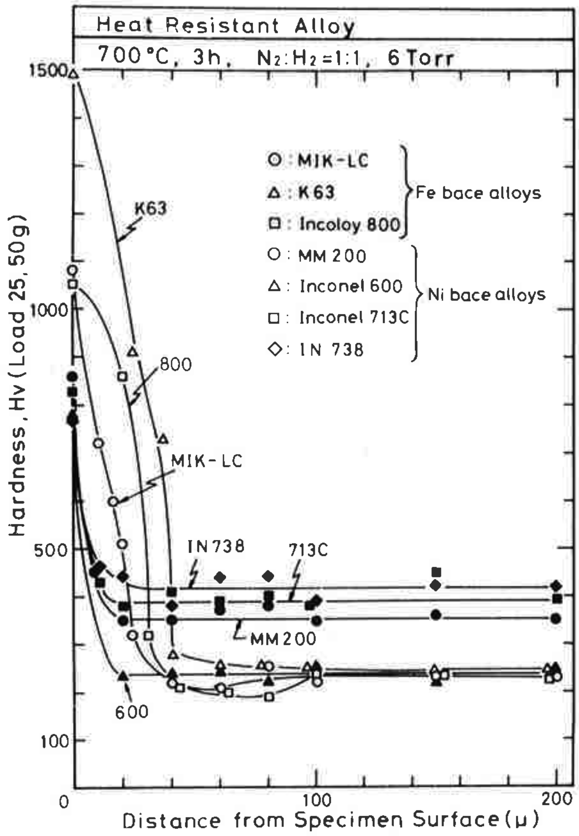

Fig. 9 Hardness distribution in cross-section of material for ferrous- and nickel-base heat resistant alloys

Table 4 Surface hardness, thickness of hardened layer and surface color tone after ion nitriding treatment for heat resistant alloys

Material		Surface hardening*	Treatment (°C)×(hrs)×(Torr)×(Gas)	Hardness (Hv)			Hardened zone** (μ)	Color after treatment+
				Surface** (Hvs)	Base (HvB)	Ratio (Hvs/HvB)		
Heat resistant alloy (Fe base)	MIC-LC	O	700×3×6×(N_2:H_2=1:1)	1080	230	4.7	30-40	SW
	K63	O		1500	240	6.3	40	SW
	Incoloy 800	O		1050	190	5.5	40	Bl
(Ni base)	Inconel 600	O	700×3×6×(N_2:H_2=1:1)	780	250	3.1	<20	Bl
	Inconel 713C	O		830	390	2.1	<20	LGr
	MM200	O		860	350	2.5	<20	LGr
	IN738	O		770	420	1.8	<20	LGr
	U-500	O	900×1×6×(N_2:H_2=1:1)	530	340	1.6	20	SW
	H-B	O		460	270	1.7	20-30	SW
(Co base)	ZCo	?	900×1×6×(N_2:H_2=1:1)	560	420	1.3	(20)	SW
	UMCo	O		430	330	1.3	20	SW

* O Yes, X No ** Approximate value
\+ SW:Silver white, BL:Black, LGr:Light gray

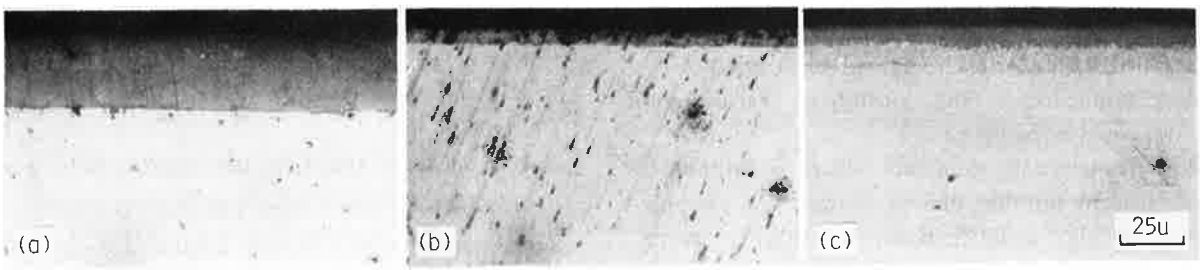

Fig. 10 Microstructure in cross-section of material for heat resistant alloy after nitriding; (a) Incoloy 800, (b) Inconel 600 and (c) UMCo

3.4 Copper and aluminum alloys

OFC (oxygen free copper), OMC (Cu-0.5% Cr-0.1% Zr), copper-4% beryllium, copper-9% aluminum, copper-10% chromium, monel (Cu-70% Ni) and some copper mother alloys were used as copper alloys, and commercial aluminum (Al) and some aluminum mother alloys were used as aluminum alloys. The results after nitriding were expressed in **Table 5**. Except Cu-4% Be alloy surface hardening of these alloys was not observed. The behavior of Be in copper for nitriding has to be paid attention hence.

Surface hardening of copper and aluminum alloys is strongly expected from industrial purposes. Therefore the surface hardening of these alloys should be researched from the other point of view.

Table 5 Surface hardness, thickness of hardened layer and surface color tone after ion nitriding treatment for copper and aluminum alloys

Material		Surface Hardening*	Treatment (°C)×(hrs)×(Torr)×(Gas)	Hardness (Hv) Surface** (Hvs)	Base (HvB)	Ratio (Hvs/HvB)	Hardened zone (μ)**	Color after treatment+
Copper alloy	OFC(Cu)	X	700 × 3 × 6 × (N_2:H_2=1:1)	70	70	1.0	-	Bl
	OMC	X		60	80	<1	-	Bl
	Cu4Be	O		310	190	1.6	40	Bl
	Cu9Al	?		220	190	1.2	(20-30)	SW
	Cu10Cr	?		100	80	1.3	(10-20)	BB
	Cu70Ni	X		150	170	<1	-	Bl
(Mother alloy)	Cu10Si	X		580	470	1.2	-	Bl
	Cu10Co	X		70	110	<1	-	BB
	Cu25Ti	?		500	420	1.2	(20)	Bl
	Cu30Zr	X		550	570	<1	-	Bl
Aluminum alloy	Al	X	500×2/3×6×(N_2:H_2=1:1)	20	32	<1	-	Gr
(Mother alloy)	Al5Ti	X		26	27	<1	-	LBG
	Al5Zr	X		31	30	1.0	-	LG
	Al5Ti1B	X		28	30	<1	-	LGr
	Al5V	X		35	26	1.3	-	LBG
	Al5Cr	X		31	36	<1	-	BGr

* O Yes, X No ** Approximate value
+ Bl:Black, SW:Silver white, BB:Blue-brown, Gr:Gray, LGr:Light gray, LG:Light gold LBG:Light blue gold, BGr:Blue gray

4. Conclusions

An ion nitriding apparatus was installed and nitriding surface hardening was tried for various commercial metals and alloys. As a result, the following conclusions were drawn;

(1) All metals and alloys in IVa, Va and VIa families in periodic table were possible to be hardened by ion nitriding process, though tungsten was not hardened in this experiment.

(2) Most iron-nickel alloys could be hardened, while nickel could not. Moreover all stainless steels used in this experiment could obviously be hardened by this process. However two different hardenable modes were observed in stainless steels, ie, one was a constant hardeness in whole hardened layer and the other was gradual decrease in hardness inwardly.

(3) Most iron-, nickel- and cobalt-base heat resistant alloys could be hardened.

(4) Most copper and aluminum alloys could not be hardened by nitriding process. However only copper-beryllium alloy could be hardened in this experiment.

(5) More detailed investigations for nitriding are needed in future for the metals and alloys which were found to have probability of surface hardening.

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