Surface Hardening of Various Metals and Alloys with Boronizing Technique†

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Abstract

By means of boronizing technique in argon atmospheric furnace at 950 – 1000°C with boron powder, probability of surface hardening has been investigated for various reactive, refractory, ferrous and nonferrous and heat-resistant metals and alloys in commercial use.

Surface hardening was possible for all these metals and alloys used. Maximum hardness on surface of most metals and alloys represented more than VHN1000. Moreover hardness distribution and microstructure in crosssectional area, and X-ray analysis of boronized layer were investigated.

These results indicated the introduction for further investigation for boronizing technique of various new alloys which will be developed.

KEY WORDS: (Surface Hardening) (Ferrous and Nonferrous Alloys) (Boronizing)

1. Introduction

Various surface hardening techniques have been developed and investigated for the purposes of improvement of metal surface against abrasion, cavitation, corrosion and so on.

Among them boronizing is one of the most feasible and reliable techniques[1].

The authors have reported, so far, two papers for boronzing possibility for the surface hardening of copper-nickel[2] and gold alloys[3]. In these papers the boronizing technique was useful for the surface hardening of these alloys.

However there are few reports published for boronizing technique in Japan and are less data for boronized surface of metals and alloys especially for nonferrous materials.

Therefore in this paper the authors have investigated for the possibility of the surface hardening for various metals and alloys by boronizing in order to obtain the wide knowledges as a preliminary study.

2. Experimental Procedure

2.1 Materials used

All materials used for boronizing are 1.5 to 2 mm thick commercial sheets. Commercial pure titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo) and tungsten (W) metals and molybdenum-titanium-zirconium (TZM) alloy as reactive and refractory metals, commercial pure iron (Fe), invar alloy of Fe-36%Ni (Fe36Ni), commercial pure nickel (Ni) and SUS 304, 310S, 316, 321, 347 austenitic and SUS 430 ferritic stainless steels as popular metals and alloys, and Incoloy 800(In-800), Inconel 600 (In-600), Udimet 500 (U-500), Hasteloy B (H-B), Stellite Z (ZCo), Co base Cr and Fe alloy (UMCo) and commercial pure cobalt (Co) as Iron-, Ni-, and Co-based heat-resistant alloys have been investigated.

2.2 Boronizing technique

Boronizing furnace and technique have been reported in the previous paper[1–2]. The boronizing temperature under argon flow was selected 950°C and 1000°C for 3 to 24 hrs.

For each material a 10 mm square × 1.5 to 2 mmt specimen in size is used for each treatment.

2.3 Investigations

After boronizing, each specimen was investigated for hardness distribution (10gf) with Micro Hardness tester, microstructure near the surface with optical and scanning

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

Table 1 Surface hardness, thickness of hardened zone and color tone after treatment for reactive and refractory metals.

Reactive & refractory metal		Surface hardening*	Treatment (°C)×(hrs)	Hardness (Hv)			Hardened zone (μ)**	Color after treatment†
				Surface** (Hvs)	Base (HvB)	Ratio (Hvs/HvB)		
(IVa)	Ti	O	1000×24	3300	200	16.5	10	G
	Zr	O		2960	160	18.5	15	LG
	Hf	O		1540	290	5.3	10	LG
(Va)	V	O	1000×6	2960	260	11.4	20	G
	Nb	O		2200	130	17.0	10	LG
	Ta	O		2700	150	18.0	30	LG
(VIa)	Cr	O	1000×6	2190	210	10.0	20	SW
	Mo	O		2410	290	8.3	30	SW
	TZM	O		2650	330	8.0	30	SW
	W	O		2250	440	5.1	30	SW

* O Yes, X No ** Approximate value
† G:Gray, LG:Light Gray, SW:Silver white

electron microscope, and X-ray analysis for determination of the surface compounds with 40 kV - 20 mA Cu Kα.

3. Experimental Results

3.1 Reactive and refractory metals and alloys

Boronizing results are shown in **Table 1** for Ti, Zr and Hf as IVa group metals in periodic table, V, Nb and Ta as Va, and Cr, Mo, TZM and W as VIa.

Surface hardening for these metals was possible at 1000°C for 6 and 24 hrs except for Ti at 1000°C for 6 hrs. Hardness of hardened surface (HVS) were extremely high as 1500 to 3300VHN and the ratio to base metal (HVB) were also obtainable within the range of 5 to 18 times. Hardened zone was 10 to 30 μm in rough estimation. The surface color of the specimens after treatment showed gray for IVa and Va, and silver white for IVa metals.

Figures 1, 2 and **3** showed the hardness distributions of these metals in crosssection after boronizing treatment.

The thickness of boronizing surface layer was generally thinner in IVa metals than Va and VIa metals. Especially Mo and W metals were easy to make a hard surfacing with boronizing technique.

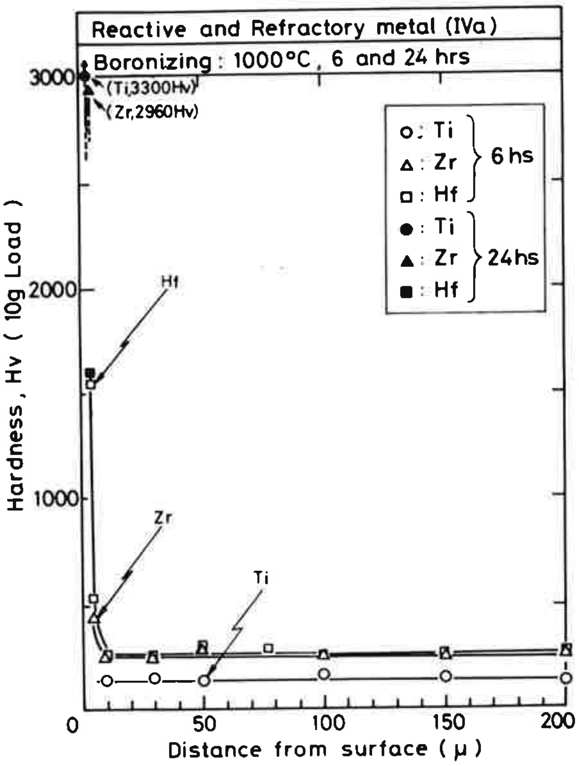

Fig. 1 Hardness distributions on crosssection of IVa-group metals after treatment.

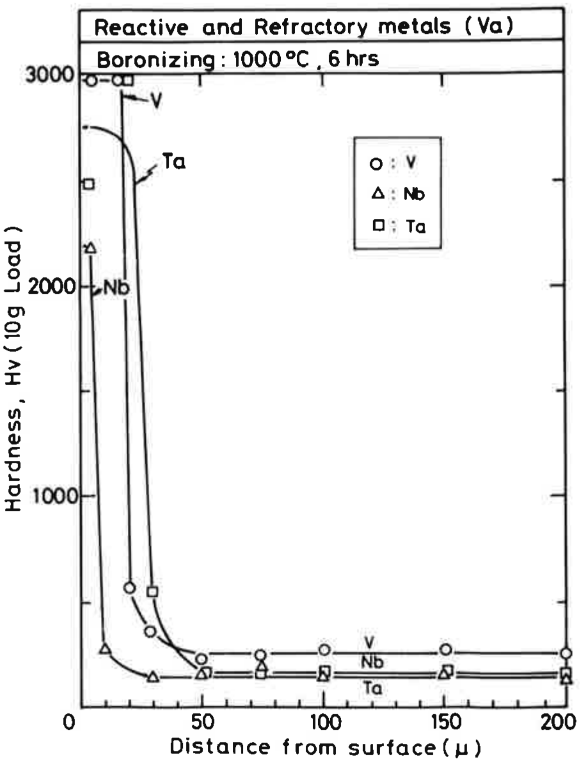

Fig. 2 Hardness distributions on crosssection of Va-group metals after treatment.

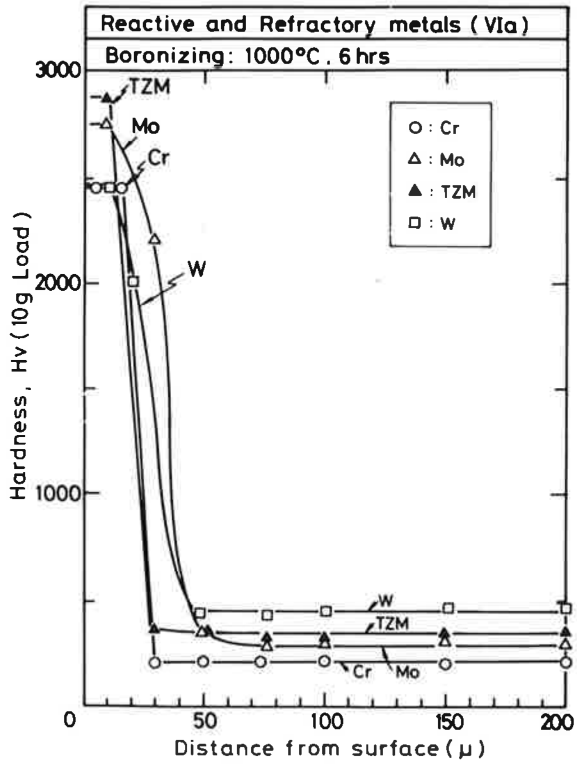

Fig. 3 Hardness distributions on crosssection of VIa-group metals and alloy after treatment.

Figure 4 (a) through (j) showed crosssection of the specimen near surface with optical microscope for Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, TZM and W, respectively, the upper side of which represented the hardened layer with boronizing. However in this boronizing condition there were some crackings at the interface between outer and inner boride layers and also between inner boride layer and matrix in VIa group metals and alloy. For these metals other boronizing condition has to select to make a sound boride layers. On the other hand, no cracking was seen in IVa and Va group metals.

Figure 5 shows an example of XMA analysis of boron in a distinct boride layer whose boron centent is apparently different was detected, although four or five boride layers exist in the Cr-B binary consitutional diagram[4].

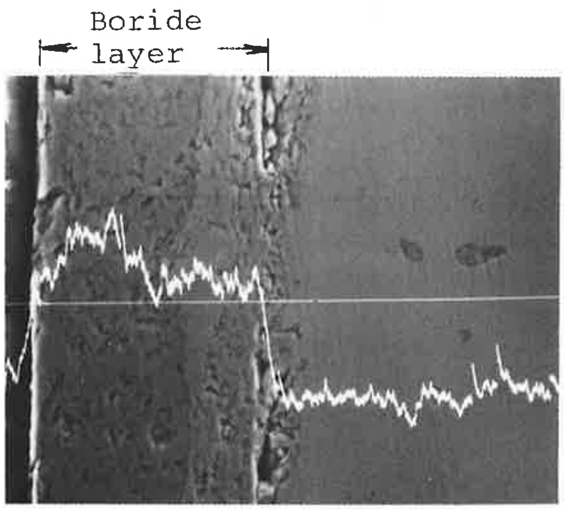

Fig. 5 Boron distribution on boronized surface layer of Cr metals after treatment of 1000°C for 24 hrs.

3.2 Iron, nickel, Fe-Ni and stainless steels

Table 2 showed the experimental results after boronizing treatment at 950°C for 3 hrs. Iron, nickel and inver

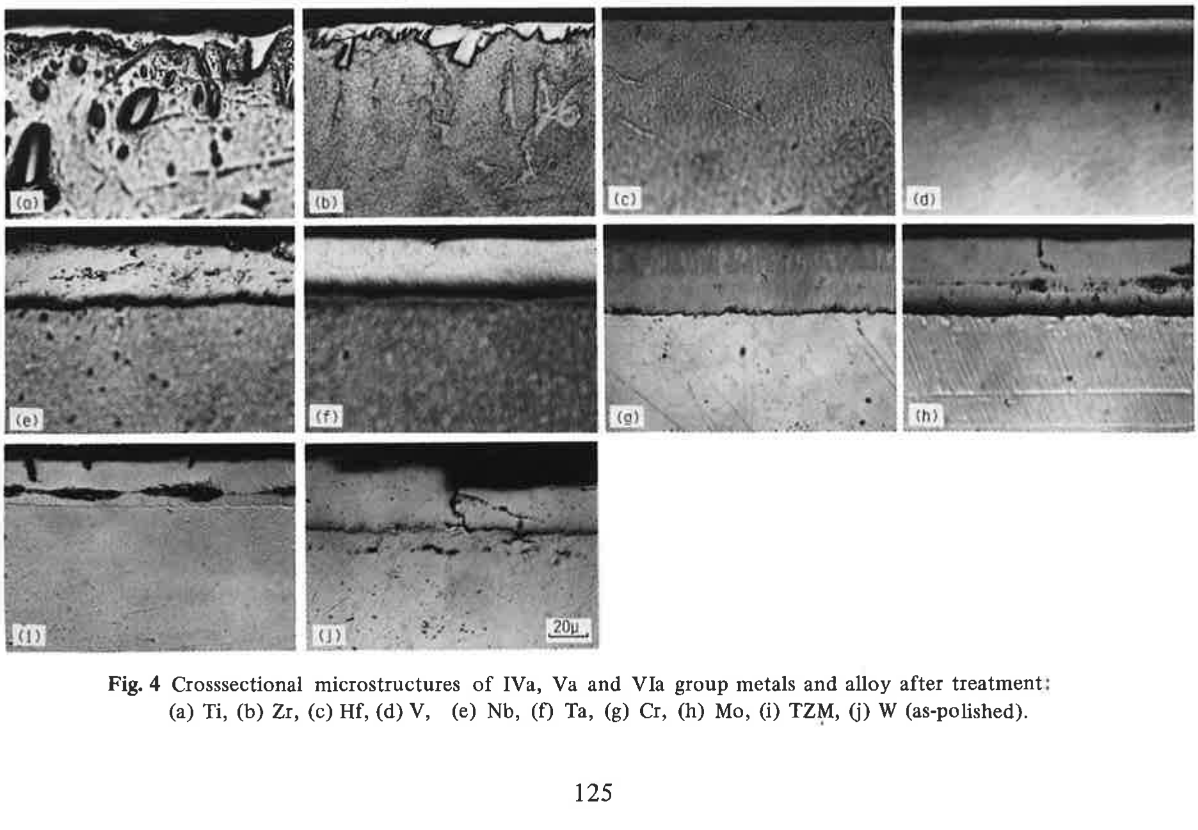

Fig. 4 Crosssectional microstructures of IVa, Va and VIa group metals and alloy after treatment: (a) Ti, (b) Zr, (c) Hf, (d) V, (e) Nb, (f) Ta, (g) Cr, (h) Mo, (i) TZM, (j) W (as-polished).

alloy, and all stainless steels were also possible for boronizing hardening.

Surface hardness of stainless steels showed about 1200 to 1600VHN and hardened layer reached to 20 to 50 μm in this treatment.

The crosssectional hardness distributions were shown in **Figs. 6** and **7** for iron and nickel group, and stainless steels, respectively.

The boronizing layer of nickel was thicker than that of iron, while the surface hardness of nickel was lower.

The macrostructure near the surface of each specimen treated was represented in **Fig. 8 (a), (b)** and **(c)** for iron and nickel group, and in **Fig. 9 (a)** through **(f)** for stainless steels, respectively.

In Fig. 8 the boride layer penetrated spiky in the matrix for iron and much porosity was seen in outer layer. While as to the stainless steels as shown in Fig. 9 the penetration of boride layer was complex and showed different fashion for type of steel. The grain boundary penetration was clearly seen in SUS 304, 310S, 316 and 321 steels, while the spiky penetration was seen in SUS 430 ferritic stainless steel. Many porosities were observed in boride layer in SUS 430 steel.

Generally the appearance of the surface after boronizing was not so smooth in stainless steels due to peel off in the outer surface.

3.3 Heat-resistant alloys

Table 3 shows the results of Fe-, Ni- and Co-base alloys after boronizing at 950°C for 3 hrs.

All of these alloys used were possible to make hard surfacing and showed the maximum hardness more than 1000 VHN which is required for industrial use. The hardened layer of these alloys reached to 20 to 50 μm. The hardness distributions were shown in **Fig. 10** for Ni-base alloys and pure nickel for reference and **Fig. 11** for Co- and Fe-base alloys.

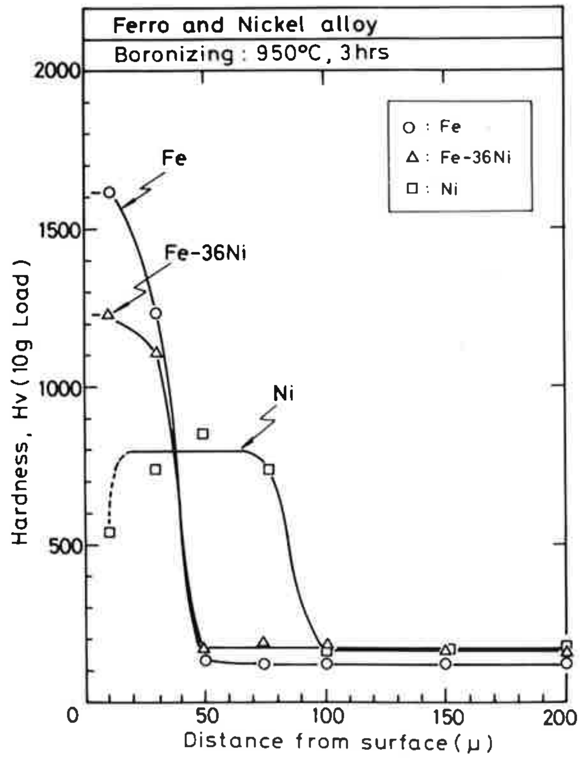

Fig. 6 Hardness distributions on crosssection of iron and nickel group after treatment of 950°C, 3 hrs.

Pure metals, both nickel and cobalt showed wider hardened layer, while they reached lower maximum hardness.

In **Fig. 12 (a)** through **(g)** microstructures of each hardened layer for these alloys were collectively shown.

For Fe- and Ni-base alloys a clear penetration of boride around grain boundaries of base metal was observed. For cobalt and Co-base alloys, however, grain boundary penetration was not clear and spiky boride layer was seen in cobalt metal.

3.4 X-ray diffractive analysis of boride surface

Table 4 shows the borides which were determined with X-ray diffractive analysis for each metal surface after

Table 2 Surface hardness, thickness of hardened zone and color tone after treatment for iron and iron-nickel alloy, and stainless steels.

Material		Surface hardening*	Treatment (°C)×(hrs)	Hardness (Hv)			Hardened zone (μ)**	Color after treatment†
				Surface** (Hvs)	Base (HvB)	Ratio (Hvs/HvB)		
Ferro & nickel alloy	Fe	O	950×3	1350	120	11.3	30	G
	Fe36Ni	O		1220	170	7.2	30	LG
	Ni	O		800	150	5.3	80	LG
Stainless steel	304	O		1600	230	7.0	20	LG
	310S	O		1480	170	8.7	30	LG
	316	O		1430	160	9.0	30	LG
	321	O		1380	170	8.1	50	LG
	347	O		1200	180	6.7	30	G
	430	O		1350	150	9.0	30	LG

* OYes, X No ** Approximate value † G:Gray, LG:Light Gray

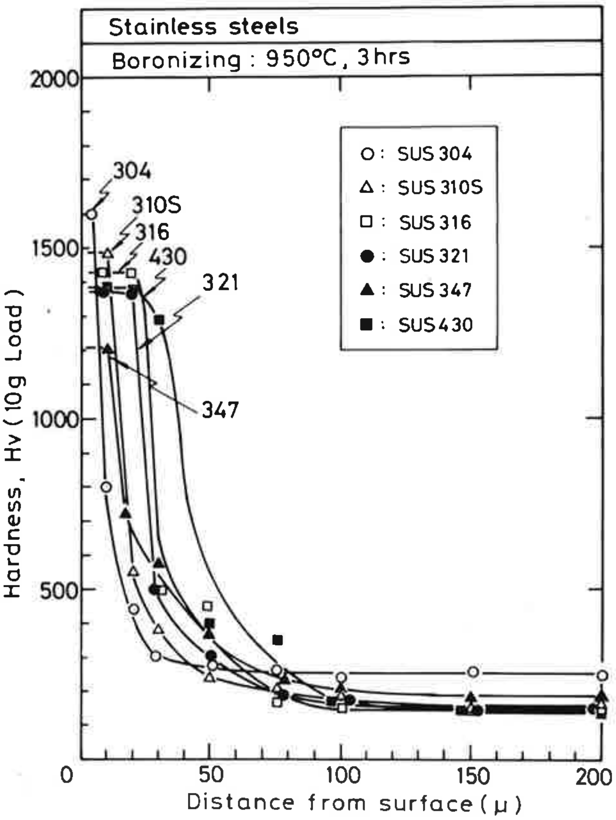

Fig. 7 Hardness distributions on crosssection of stainless steels after treatment of 950°C, 3 hrs.

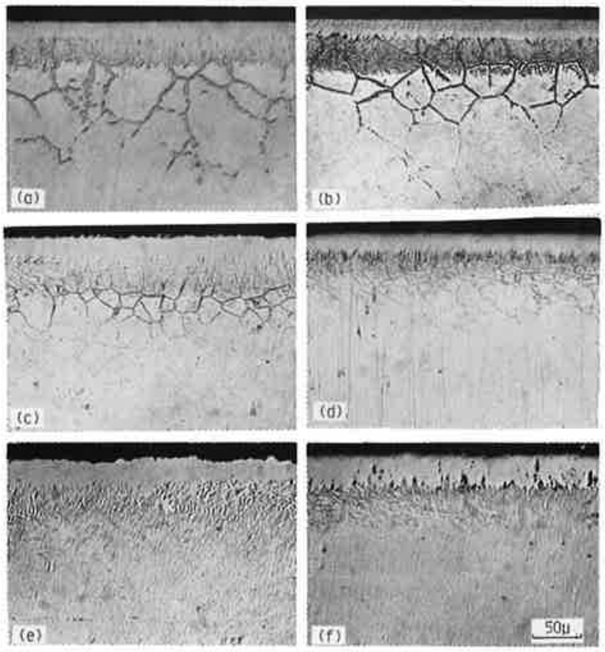

Fig. 9 Crosssectional microstructures of stainless steels after treatment of 950°C, 3 hrs: (a) SUS 304, (b) SUS 310S, (c) SUS 316, (d) SUS 321, (e) SUS 347 and (f) SUS 430 (as-polished).

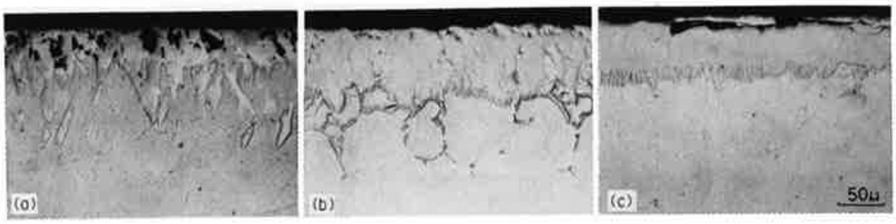

Fig. 8 Crosssectional microstructures of iron and nickel group after treatment of 950°C, 3 hrs: (a) Fe, (b) Fe-36%Ni, (c) Ni (as-polished).

Table 3 Surface hardness, thickness of hardened zone and color tone after treatment for Fe-, Ni- and Co-base heat-resistant alloys.

Heat resistant alloy		Surface hardening*	Treatment (°C)×(hrs)	Hardness (Hv)			Hardened zone** (μ)	Color after treatment+
				Surface** (H_{VS})	Base (H_{VB})	Ratio (H_{VS}/H_{VB})		
Fe base	Incoloy 800	O	950×3	1190	180	6.6	40	LG
Ni base	Inconel 600	O		1030	190	5.4	20	SW
	U-500	O		1070	230	4.6	40	LG
	H-B	O		1410	210	6.7	30	LG
Co base	ZCo	O		1400	490	2.9	30	G
	UMCo	O		1900	370	6.6	20	LG
	Co	O		1300	290	4.5	50	LG

* O Yes, X No **Approximate value + G:Gray, LG:Light gray, SW:Silver white

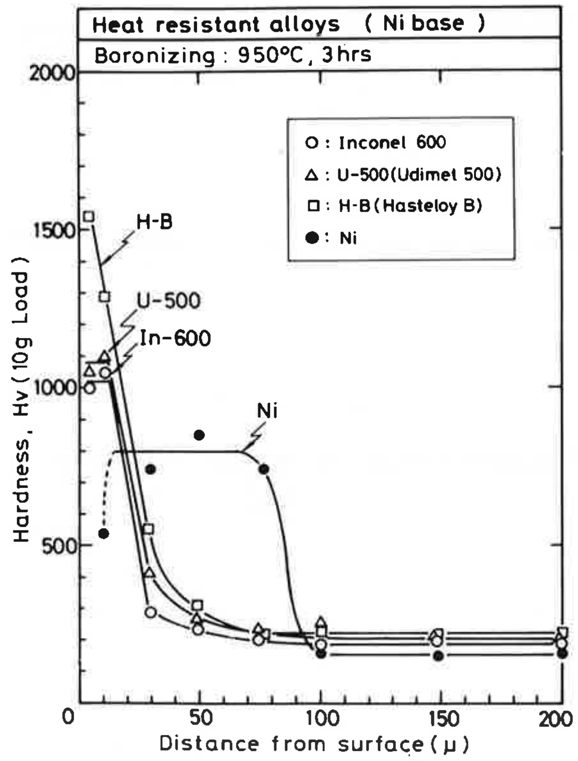

Fig. 10 Hardness distributions on crosssection of Ni-base heat-resistant alloys and pure Ni after treatment of 950°C, 3 hrs.

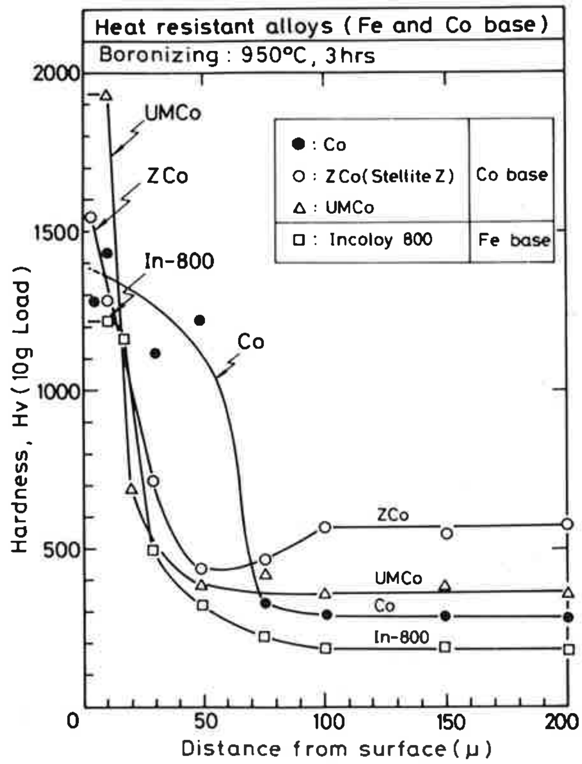

Fig. 11 Hardness distributions on crosssection of Co- and Fe-base heat-resistant alloys after treatment of 950°C, 3 hrs.

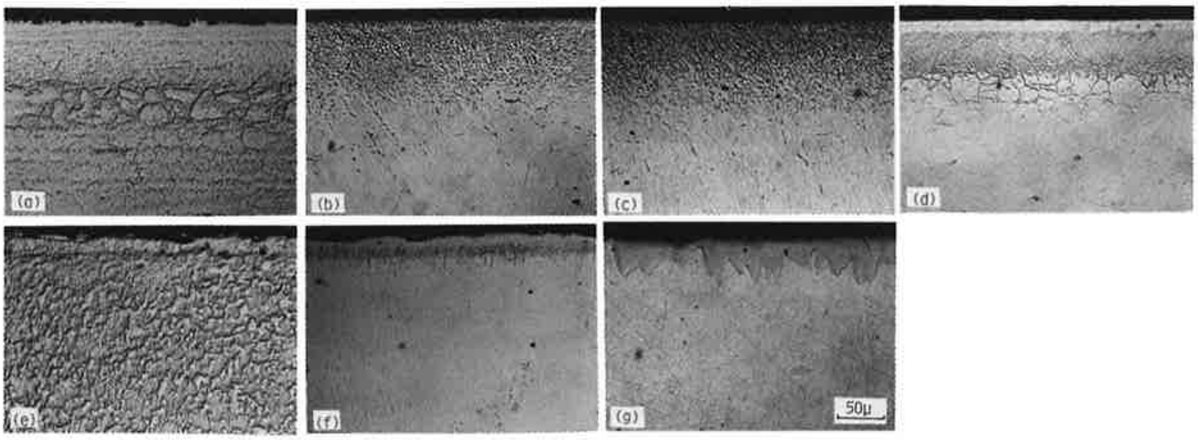

Fig. 12 Crosssectional microstructures of Fe-, Ni- and Co-base heat-resistant alloys after treatment of 950°C, 3 hrs: (a) In-800, (b) In-600, (c) U-500, (d) H-B, (e) ZCo, (f) UMCo, (g) Co (as-polished).

boronizing. Boride compound was detected for all metals. For Zr, Hf, V, Nb, Ta, Cr, Co and Ni metals single boride was only detected, though several boride phases are reported to be formed according to binary constitutional diagrams[4]. One reason why single boride was only detected seems to be due to the direction of X-ray irradiation which was from surface of the specimen. For the determination of the boride layer formed and its composition are expected for further investigation.

4. Conclusions

Boronizing surface hardening was tried for various commercial metals and alloys. As a result the following conclusions were drawn;

(1) All materials in IVa, Va and VIa groups in periodic table were possible to be hardened by boronizing technique at 1000°C for 6 or 24 hrs. The maximum hardness for these metals on the surface were very high as 1500 to 3300VHN. However some of them showed surface crack and porosities in the boride layer. Therefore for industrial uses further investiga-

Table 4 Boride phases detected with X-ray diffractive analysis from boronized surface of various pure metals.

Metal	Boride	Treatment
Ti	TiB_2, TiB	1000°C 24hrs
Zr	ZrB_2	
Hf	HfB_2	
V	VB_2	1000°C 6hrs
Nb	NbB_2	
Ta	TaB_2	
Cr	CrB_2	
Mo	Mo_2B_5, δ-MoB	
W	WB, W_2B	
Fe	FeB, Fe_2B	950°C 3hrs
Co	Co_2B	
Ni	Ni_2B	

tions will be needed for boronizing conditions.

(2) Iron, Inver alloy (36%Ni-Fe) and all stainless steels were possible to be hardened by the boronizing technique at 950°C for 3 hrs. The maximum hardnesses for the alloys reached to more than 1000VHN. This high hardness will be much interested in the industrial field.

(3) Heat-resistant alloys of Fe-, Ni- and Co-based were also possible to be hardened by the boronizing technique at 950°C for 3 hrs. The maximum hardnesses more than 1000VHN were obtained for the surface and the hardened layers more than 20 μm were easy to make. This will be useful for the uses of industrial purposes.

(4) Microstructural investigations and X-ray analysis for boride layer were studied for all the metals used. Further investigations will be required to determined the composition and structure of whole boride layers.

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