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# Surface Hardening of Gold with Boronizing Technique†

Fukuhisa MATSUDA\*, Kazuhiro NAKATA\*\*, Kenji TOHMOTO\*\*\* and Masaki MORIKAWA\*\*\*\*

## Abstract

Surface hardening of gold containing Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, Fe, Co or Ni elements was tried by means of boronizing technique with powder boron under argon atmospheric furnace at 900 to 950°C for mainly 6 hrs.

The obvious surface hardening was possible for the gold alloy which contains alloying element more than 5%Ti, 5%V, 3%Cr, 15%Mn, 10%Fe, 5%Co or 5%Ni. Surface hardness in maximum and thickness of the hardened layer strongly depended on alloying element added and showed more than 3000 VHN (micro) and up to 10 $\mu$ m for Au-Ti, 1900 and 10 $\mu$ m for Au-V, 1500 to 1600 and up to 20 $\mu$ m for Au-Cr, 2100 and 30 $\mu$ m for Au-Mn, 900 to 1000 and up to 80 $\mu$ m for Au-Fe, 1500 and up to 50 $\mu$ m for Au-Co, and 600 to 700 and up to 50 to 70 $\mu$ m for Au-Ni alloys.

Moreover the phases formed on the hardened surface were investigated in aid of X-ray diffractive analysis.

**KEY WORDS:** (Surface Hardening) (Gold and Gold Alloys) (Boronizing) (Boriding) (Boron) (Precipitation) (Diffusion)

## 1. Introduction

Gold has been utilized as materials for decorative, dental and industrial purposes besides as amassed wealth.

Recently the use of gold for the purposes of the materials is gradually increased, for example, jewelry, personal ornaments, watches, spectacles, writing pens, artificial teeth, bonding wire in integrated circuits, special switches and so on.

Gold has many excellent characters and among them softness in hardness is one of the outstanding features for making foils and processing to complex shape. However softness is simultaneously one of the inevitable faults in golden goods because the surface of the valuable goods is easy to be get shallow or severe wounds. The wounds on the surface frequently lowered the value of the golden goods.

Therefore the surface hardening of gold whose hardness is considerable hard is one of the expected technologies in this field. However the technology of the surface hardening of gold has not been developed so far within the authors' knowledges.

The authors have tried to develop the technology which hardens the surface of gold by means of boronizing method. This is one of alloying methods to the surface of alloy by diffusive penetration of solid boron element and hence the thickness of hardened layer is expected to be about 10 to 100  $\mu$ m which is usually thicker than those of CVD or PVD plating or coating.

In this report the techniques of the surface hardening of gold which were tried by the authors are introduced.

## 2. Fundamentals of the technology

It was impossible to make a hardened layer on the surface of K24 pure gold by means of boronizing process in the preliminary investigation in advance. Accordingly the authors have considered that it would be possible to make a hardened layer on the gold surface if some alloying element which has a strong affinity with boron is added in K24 pure gold. The mechanism is imagined as shown in Fig. 1. When gold metal in which some alloying atoms is added as shown in (○) mark is contact at its surface with boron powder, black zone, in high temperature environment, the boron atoms (●) mark, will diffuse to the gold metal and combine with alloying atoms. As a result, the hardened layer will be made on or near the gold surface.

Subsequently as far as the alloying element in gold is

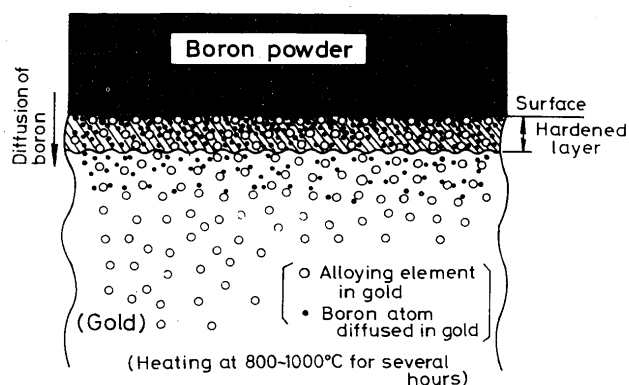


Fig. 1 Schematic illustration showing the mechanism of surface hardening of gold alloy by boronizing technique

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concerned, the less it contains, the better for gold. Therefore the element should be selected from standpoint of thermodynamic chemical affinity with boron.

After the investigations with the references<sup>1-3</sup>, the metals whose free energies of their borides are listed in Table 1 were nominated as strong reactive elements with boron. Moreover the solubility of these elements in gold is estimated from binary equilibrium constitutional diagrams<sup>4-5</sup> at room temperature and 900°C in Table 2. Therefore the authors have investigated for boronizing characteristics of those eleven different gold alloy systems.

**Table 1** Formation energies of borides of alloying elements at 900°C

Group in the Periodic Table	Reaction	ΔG(Kcal/mol) at 900°C		
		Г.Б.ЗЕМЦОВ <sup>1)</sup>	Е.Т.Туркдоган <sup>2)</sup>	С.Охмори <sup>3)</sup>
IVa	$\frac{1}{2}\text{Ti} + \text{B} = \frac{1}{2}\text{TiB}_2$	-35	-31.1	-
	$\text{Ti} + \text{B} = \text{TiB}$	-40	-37.4	-
	$\frac{1}{2}\text{Zr} + \text{B} = \frac{1}{2}\text{ZrB}_2$	-	-35.9	-
	$\frac{1}{2}\text{Hf} + \text{B} = \frac{1}{2}\text{HfB}_2$	-	-38.4	-
Va	$\text{V} + \text{B} = \text{VB}$	-	-31.4	-
	$\frac{1}{2}\text{Nb} + \text{B} = \frac{1}{2}\text{NbB}_2$	-	-28.7	-
	$\frac{1}{2}\text{Ta} + \text{B} = \frac{1}{2}\text{TaB}_2$	-	-23.7	-
VIa	$\frac{1}{2}\text{Cr} + \text{B} = \frac{1}{2}\text{CrB}_2$	-16	-9.8	-
	$\text{Cr} + \text{B} = \text{CrB}$	-17	-16.1	-
VIII	$\text{Fe} + \text{B} = \text{FeB}$	-14	-16.1	-15.5
	$2\text{Fe} + \text{B} = \text{Fe}_2\text{B}$	-	-15.8	-18.6
	$\text{Co} + \text{B} = \text{CoB}$	-	-20.9	-
	$2\text{Co} + \text{B} = \text{Co}_2\text{B}$	-	-28.0	-18.8
	$3\text{Co} + \text{B} = \text{Co}_3\text{B}$	-	-	-19.6
	$\text{Ni} + \text{B} = \text{NiB}$	-18	-39.7	-
	$\frac{4}{3}\text{Ni} + \text{B} = \frac{1}{3}\text{Ni}_4\text{B}_3$	-	-22.2	-
	$2\text{Ni} + \text{B} = \text{Ni}_2\text{B}$	-	-	-17.1
	$3\text{Ni} + \text{B} = \text{Ni}_3\text{B}$	-	-	-19.3

**Table 2** Solid solubility of alloying elements in gold at room temperature and 900°C, and structures over solid solubility estimated from phase diagram

Element	Solid solubility in Au (wt%)		Structure over solid solubility
	Room temp.	900°C	
Ti	<0.45	<2	Au(α) + TiAu <sub>6</sub>
Zr	<0.35	2.9	Au(α) + ZrAu <sub>3</sub>
Hf	-	-	-
V	<4	≈5	-
Nb	-	-	-
Ta	-	-	-
Cr	<6	<14	Au(α) + Cr(α)
Mn	≈5	≈10	Au(α) + MnAu <sub>2</sub>
Fe	<3	<26	Au(α) + Fe(α)
Co	<0.1	≈5	Au(α) + Co(α)
Ni	<2	100	Au(α) + Ni(α)

- No data were obtained

**Table 3** Chemical compositions of gold alloys used in this experiment

Alloy (Au-X)	Content of alloying element (wt%)	Group in Periodic Table
Au - 2Ti 5Ti	2.34 5.09	IVa
Au - 5Zr 5Hf	5.73 4.88	Va
Au - 3V 5V 10V 18V	3.05 5.02 9.96 18.55	Va
Au - 5Nb 10Ta	4.68 9.74	VIa
Au - 1Cr 3Cr 5Cr 7Cr 10Cr	1.01 2.97 5.01 6.48 9.49	VIa
Au - 7Mn 10Mn 15Mn	6.89 9.87 15.39	VIIa
Au - 1Fe 3Fe 5Fe 10Fe 20Fe 30Fe	1.12 3.01 4.94 11.04 20.18 31.30	VIII
Au - 5Co 10Co 20Co 30Co	5.11 9.21 20.13 30.48	VIII
Au - 5Ni 10Ni 17Ni* 20Ni 35Ni	4.93 10.29 17.00 19.99 35.60	VIII

\* K18 white gold which contains 7.85 wt% palladium

30% for iron (Fe), 5 to 30% for cobalt (Co) and 5 to 35% for nickel (Ni). These elements were divided into five groups according to Periodic Table of the Elements. In Au-Ni alloy Au-17Ni alloy contains 7.85% of palladium (Pd) and is commercially used as K18 white gold. The nominal contents of gold alloys are roughly the same as actual contents as shown in Table 3.

Each alloy was melted and solidified as a button-like ingot of about 10 gram with tungsten-arc melting in an argon atmospheric chamber after premixing of K24 gold and pure alloying metal. Then the ingots were hot rolled to about 1 mm thick sheets in each stainless steel sheath. The specimen for boronizing was cut from the sheet to about 10 mm wide, 5 mm long in size.

### 3.2 Boronizing process

A polished specimen of each gold alloy was set in amorphous boron powder (0.1 to 1.0 μm diam.) of 96.6%B in a carbon crucible (25 mm diam). Subsequently as shown in Fig. 2 the crucible was fed in electrically heated furnace under argon shielding gas flow of 2l/min<sup>6)</sup>. The temperature of the specimen heated was measured in the bottom of the crucible with a 0.5 mm diam Pt-Pt.Rh thermocouples.

## 3. Experimental Procedures

### 3.1 Gold alloys used

Gold alloys used in this investigation were shown in Table 3. Nominal contents of alloying element in K24 gold was 2 and 5wt% for titanium (Ti), 5% for zirconium (Zr), 5% for hafnium (Hf), 3 to 18% for vanadium (V), 5% for niobium (Nb), 10% for tantalum (Ta), 1 to 10% for chromium (Cr), 7 to 15% for manganese (Mn), 1 to

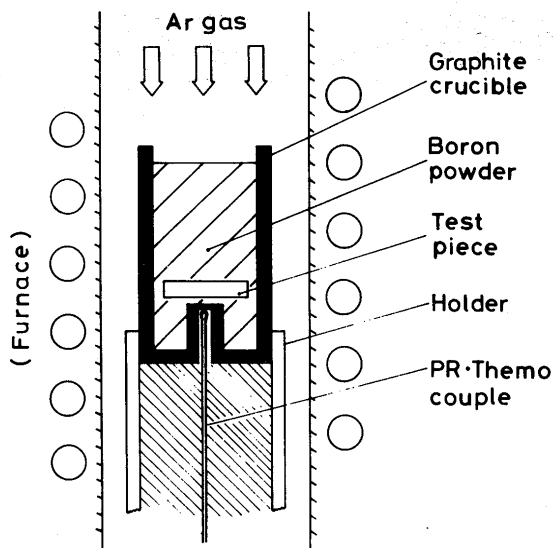


Fig. 2 Schematic illustration of boronizing process used

The boronizing treatment was done at  $950^{\circ}\text{C}$  for all Au-X (X: alloying element) systems except Au-Ni system at  $900^{\circ}\text{C}$  by the reason of lowering melting temperature, and 6 hrs except Au-Ti system for 48 hrs. Moreover, in order to investigate the start of the boronizing reaction the boronizing treatment at 800, 850 and  $900^{\circ}\text{C}$  were done for some Au-7Cr and Au-35Ni alloys.

After boronizing treatment each specimen was investigated for determination of the formation of boronizing layer with metallography and X-ray diffraction, and for hardness distribution in depth of the surface layer.

Some specimens were also investigated for distribution of element by XMA. All hardness tests were under a 25 gr load using Microvickers Hardness Tester. X-ray diffractive analyses were done with 35 kV, 30 kV and 40 kV accelerating voltage tubes with copper, cobalt and chromium targets respectively.

#### 4. Experimental Result and Discussion

##### 4.1 Hardness and metallographic investigations

###### (1) Au-Ti, Au-Zr and Au-Hf alloys (IVa group)

For the treatment of  $950^{\circ}\text{C}$ , 6 hrs, Au-2Ti, Au-5Ti, Au-5Zr and Au-5Hf alloys did not show any obvious hardened layer near surface though Au-5Ti has very thin compound layer at surface and Au-5Zr and Au-5Hf have many small compound particles near surface. Additional treatment was done for 48 hrs at  $950^{\circ}\text{C}$  for Au-5Ti. As a result Au-5Ti showed an obvious hardened layer near surface. The crosssectional hardness distribution of Au-5Ti after 48 hrs' treatment is shown in Fig. 3 in which the distance from the alloy surface and the hardness represent in abscissa and ordinate, respectively.

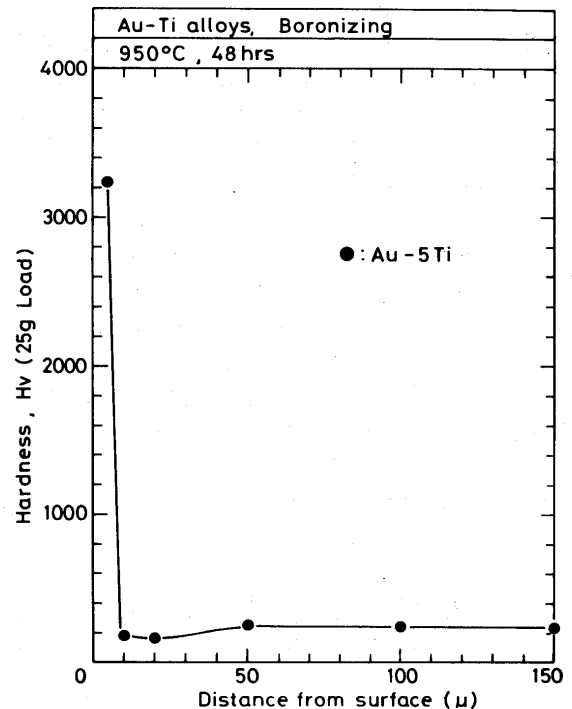


Fig. 3 Crosssectional hardness distribution for Au-5Ti alloy after 48 hrs' treatment at  $950^{\circ}\text{C}$

The maximum hardness and the thickness of hardened layer is more than 3200 VHN and less than  $10\text{ }\mu\text{m}$ , respectively. The crosssectional structure in SEM was shown in Fig. 4 in which the hardened layer (dark zone) was observed near the surface in upper side.

Judging from the authors' experiment Au alloys which contain Ti, Zr or Hf alloying elements are relatively difficult to be hardened although the affinity of these elements to combine with boron is very strong as shown in Table 1. According to the crosssectional microscopical observation for these alloys after 6 hrs' boronizing, the boronizing layer for Au-Ti alloy was too thin to evaluate

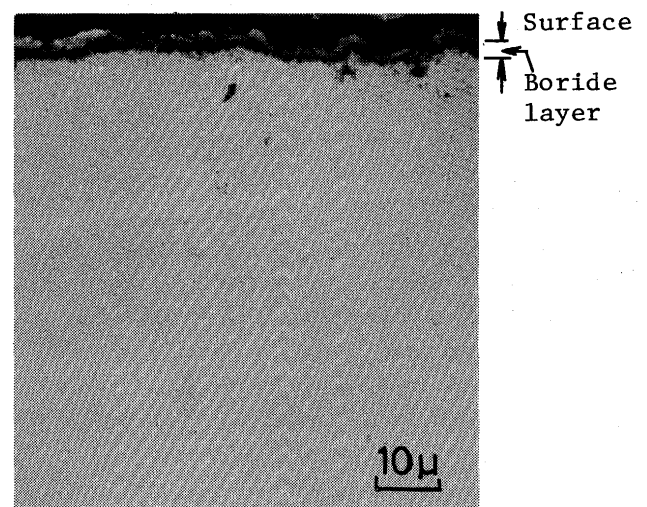


Fig. 4 Crosssectional structure in SEM of Au-5Ti alloy after treatment

the hardness, and the boride particles were dispersed extensively under the surface for Au-Zr and Au-Hf alloys, although hardness near the surface was not increased.

However, the reason why the alloying of these elements is not so effective for surface hardening is unexplainable at the present.

### (2) Au-V, Au-Nb and Au-Ta alloys (Va group)

For the treatment of 950°C, 6 hrs Au-V alloys whose V content is more than 5% showed an obvious hardened layer, while Au-3V, Au-5Nb and Au-10Ta did not.

The crosssectional hardness distribution of Au-V alloys is shown in Fig. 5 in which more than 1500 VHN and about 10  $\mu$ m hardened layer is seen for Au-10 and -18V alloys. Figure 6 shows the crosssectional metallography of Au-10V alloy after treatment.

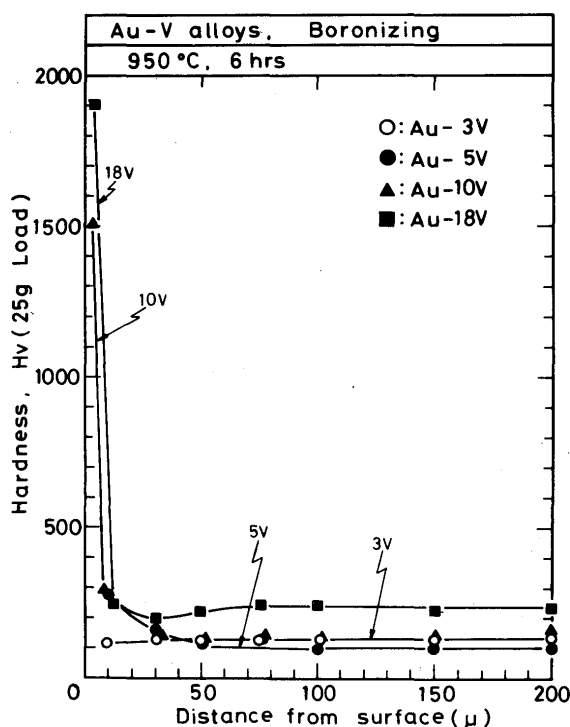


Fig. 5 Crosssectional hardness distribution for Au-V alloys after treatment

### (3) Au-Cr alloy (VIa group)

Figure 7 shows the crosssectional hardness distributions for Au-Cr alloys after the treatment 950°C, 6 hrs. Obvious surface hardening was seen in Au alloys more than Au-3Cr, but not in Au-1Cr alloy. The maximum hardness near the surface of Au-Cr alloys is about 1500 to 1600 VHN notwithstanding amount of Cr in gold and the thickness of the layer is about 10 to 20  $\mu$ m.

Figure 8 shows the crosssectional structure in SEM for Au-7Cr alloy after the treatment. The boride layer is clearly seen as a kind of flat top in which the tooth-like

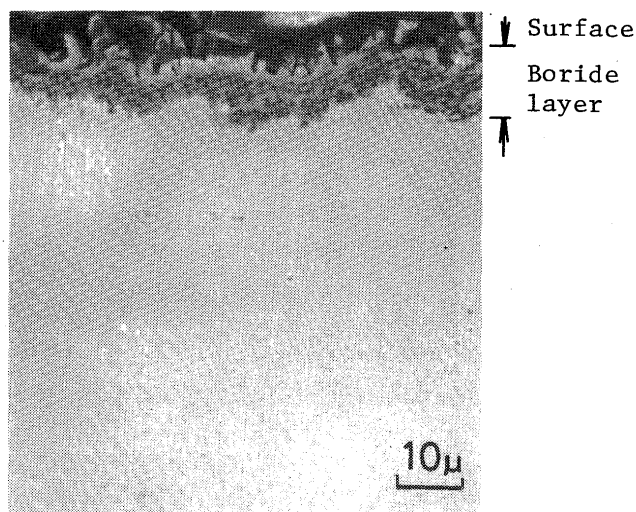


Fig. 6 Crosssectional structure in SEM of Au-10V alloy after treatment

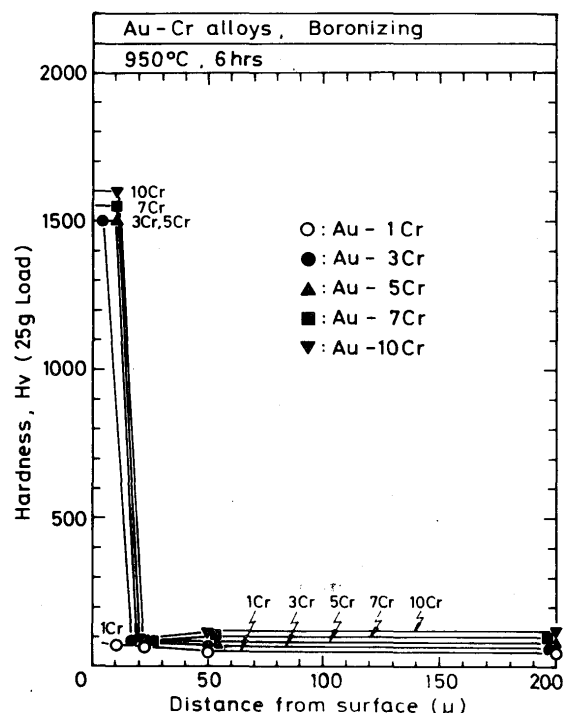


Fig. 7 Crosssectional hardness distribution for Au-Cr alloys after treatment

interface shows between the layer and the base alloy. Figure 9 shows the result of element analysis with EPMA for Au-3Cr alloy. Upper left is the secondary emission image in crosssection and upper right, lower left and lower right are distribution of Au, B and Cr, respectively. In the boride layer of hardened zone less gold and much B and Cr are seen in these figures.

### (4) Au-Mn alloy (VIIa group)

Figure 10 shows the crosssectional hardness distributions for Au-Mn alloys after the treatment. Obvious

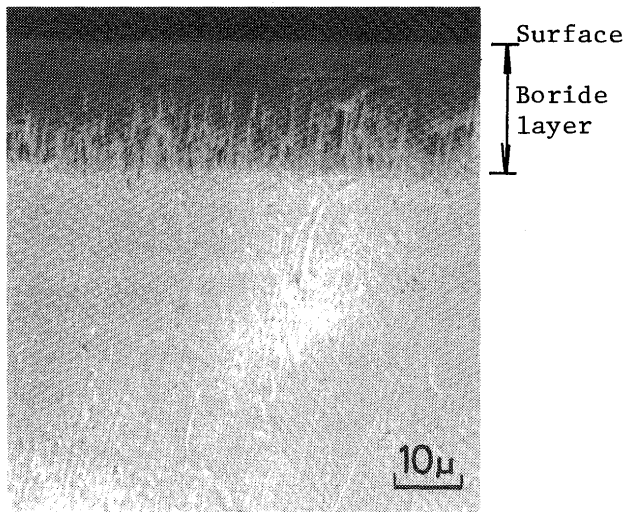


Fig. 8 Crosssectional structure in SEM of Au-7Cr alloy after treatment

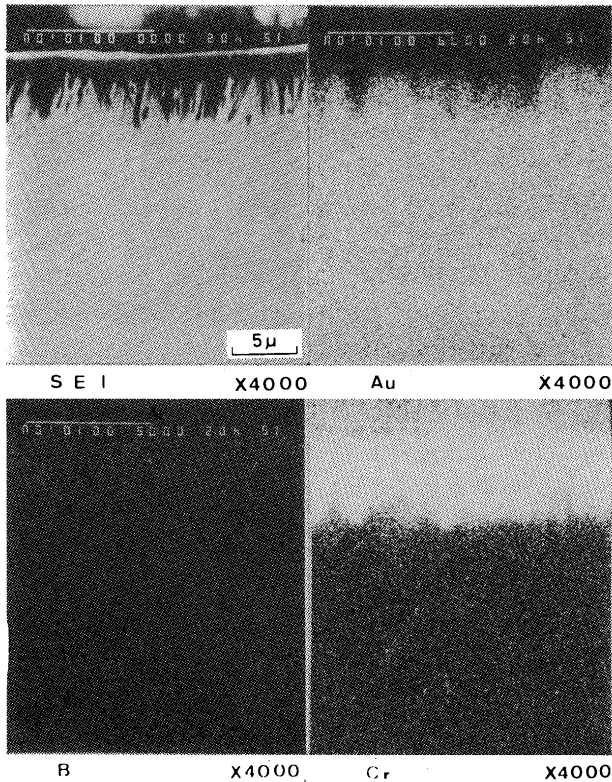


Fig. 9 Distributions of Au, B and Cr in crosssectional structure of Au-3Cr alloy after treatment

surface hardening was seen in Au-15Mn alloy, but not in Au-10 and 7Mn alloys.

The maximum hardness near the surface was about 2100 VHN and the hardened zone was about 30  $\mu\text{m}$  in thickness in which extreme hard zone of about 10  $\mu\text{m}$  and gradual hard decreasing zone of about 20  $\mu\text{m}$  were included. Figure 11 shows the crosssectional structure in SEM for Au-15Mn alloy after the treatment in which the flat boride layer is seen.

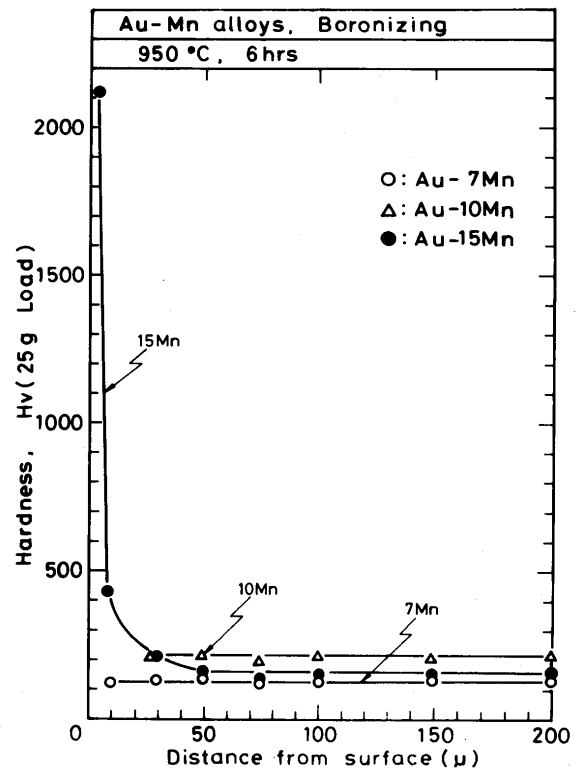


Fig. 10 Crosssectional hardness distribution for Au-Mn alloys after treatment

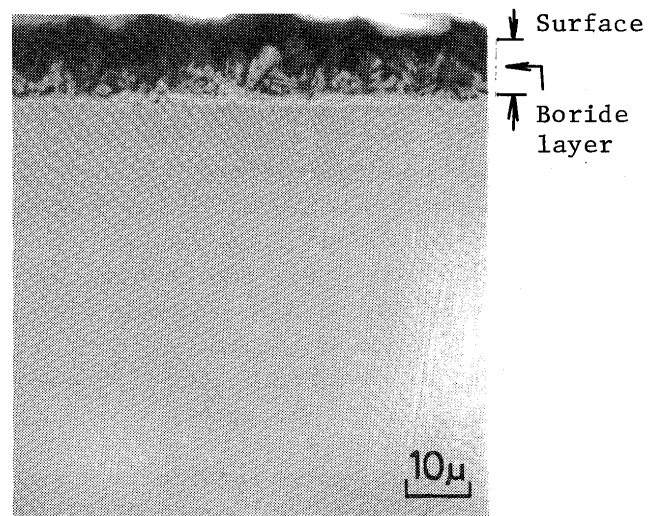


Fig. 11 Crosssectional structure in SEM of Au-15Mn alloy after treatment

#### (5) Au-Fe, Au-Co and Au-Ni (VIII group)

These gold alloys which contain Fe, Co or Ni were relatively easy to be made surface hardening with boronizing technique.

Figure 12 shows the crosssectional hardness distributions for Au-Fe alloys after the treatment. Obvious surface hardening was seen in the alloys more than 10Fe. In Au-Fe alloys the maximum hardness in the hardened layer showed about 900 to 1000 VHN and the thickness was

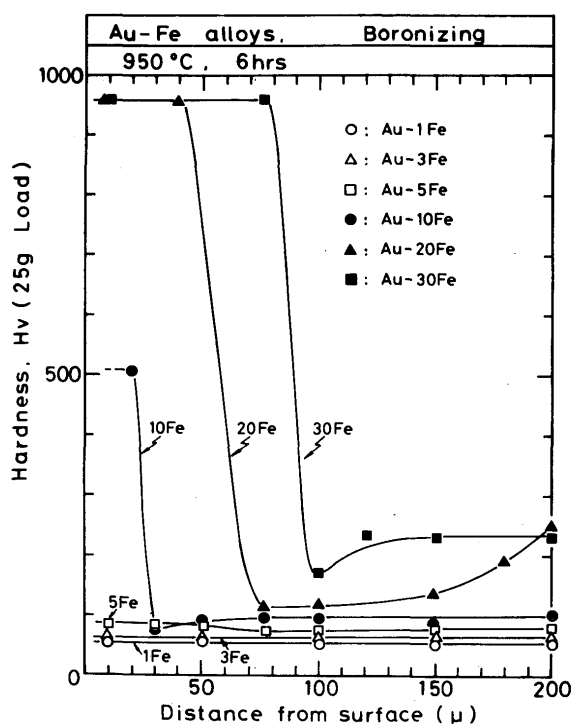


Fig. 12 Crosssectional hardness distributions for Au-Fe alloys after treatment

the deepest of all Au alloys in this experiment. In Au-1, 3 and 5Fe alloys, many small-sized precipitates were seen near the surface zone, while there is no hardness increase. Figure 13 (a), (b) and (c) show the crosssectional structure in SEM for Au-5, 10 and 30Fe alloys after the treatment. The hardened zone, which is colored as shallow gray, is dense near the surface and is insulately dispersed in the grains in the inside and spiking inwards along grain boundaries. This tendency is much clear in Au-30Fe alloy.

Figure 14 shows the crosssectional hardness distributions for Au-Co alloys after the treatment. Obvious surface hardening was seen in gold alloys more than 5Co. In Au-Co alloys the hardened layer showed 1500 VHN in the maximum hardness at the surface and gradually decreased in hardness inwardly.

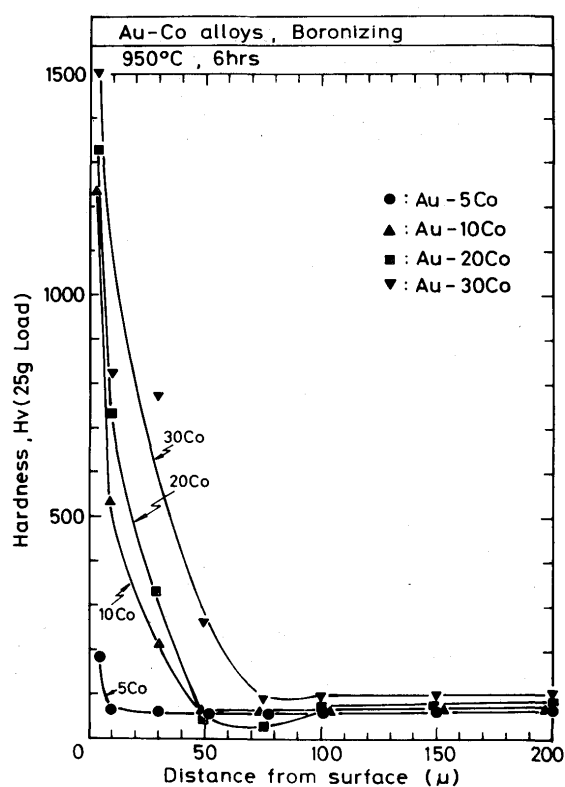


Fig. 14 Crosssectional hardness distributions for Au-Co alloys after treatment

Figure 15 (a), (b) and (c) show the crosssectional structure in SEM for Au-5, 10 and 30Co alloys after the treatment. The dense hardened layer is seen at the surface and many hardened islands are dispersed inwards.

Figure 16 shows the crosssectional hardness distributions for Au-Ni alloys after the treatment of 900°C, 6 hrs. Obvious surface hardening was seen in the alloys more than 5Ni.

The maximum hardness and the thickness of hardened zone reached about 600 to 700 VHN and about 50 μm, respectively, for Au-17, 20 and 35Ni alloys. Moreover in Au-10, 20 and 35Ni alloys the denude soft zone, which is due to decreasing of Ni, is clearly observed in succession

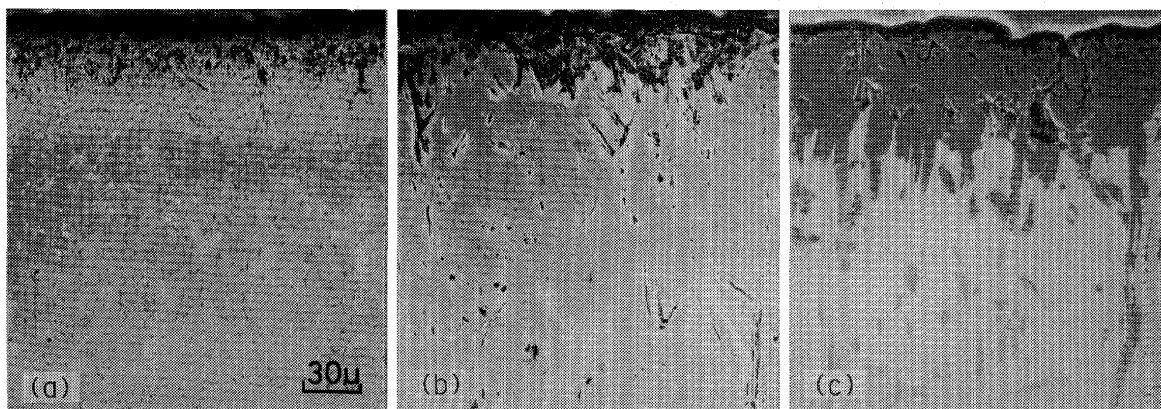


Fig. 13 Crosssectional structure in SEM of Au-Fe alloys after treatment  
(a) Au-5Fe, (b) Au-10Fe, (c) Au-30Fe



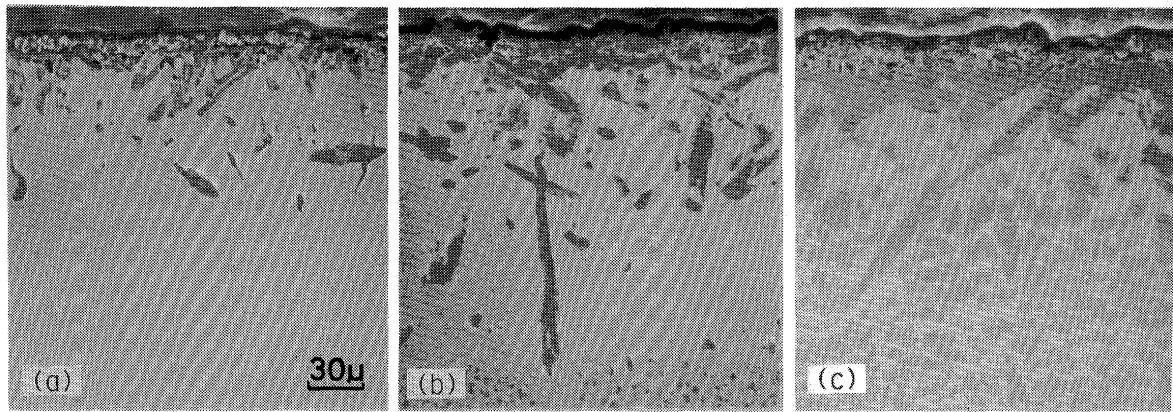


Fig. 15 Crosssectional structure in SEM of Au-Co alloys after treatment  
(a) Au-5Co, (b) Au-10Co, (c) Au-30Co

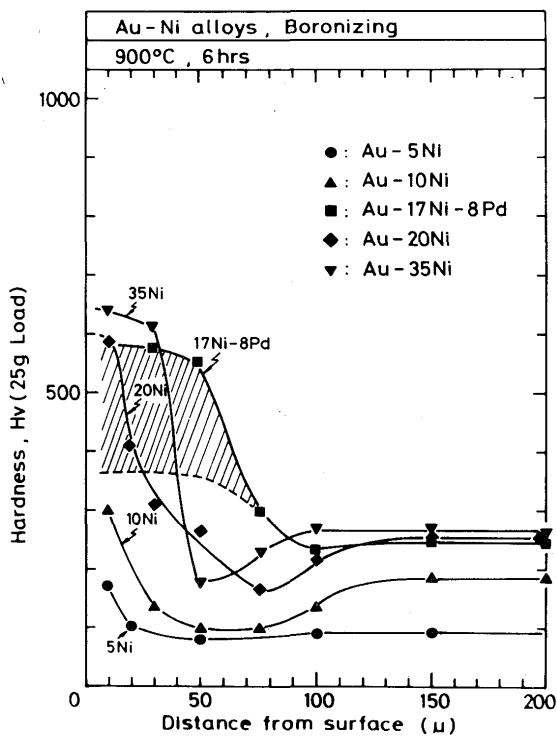


Fig. 16 Crosssectional hardness distributions for Au-Ni alloys after treatment

to hardened zone, but in Au-17Ni-8Pd alloy it is not so clear. Exceptionally in Au-17Ni-8Pd alloy a considerable scatter in hardness is seen near the surface. It is due to the mixture of large hardened precipitates and soft base constituents.

Figure 17 (a), (b) and (c) show the crosssectional structure in SEM for Au-5, 10 and 35Ni alloys after the treatment. In Au-Ni binary alloys (a), (b) and (c), as increase in Ni content, the precipitates of boride become more dense, and Au-35Ni alloy shows the dense boride layer though the thickness become thinner.

The denude zone is seen in (c) between hardened boride zone and base metal.

#### 4.2 Marginal amount of alloying element for hardening

Figure 18 shows collectively the effect of amount of alloying element on the maximum hardness near the surface of various gold alloys after the boronizing treatment. The marginal amount of alloying element which starts to increase the surface hardness with boronizing is estimated from Fig. 18 in between 2 and 5 Ti, 5 and 10 V, 1 and 3 Cr, 10 and 15 Mn, 5 and 10 Fe, 5 and 10 Co and 5 and 10 Ni alloys.

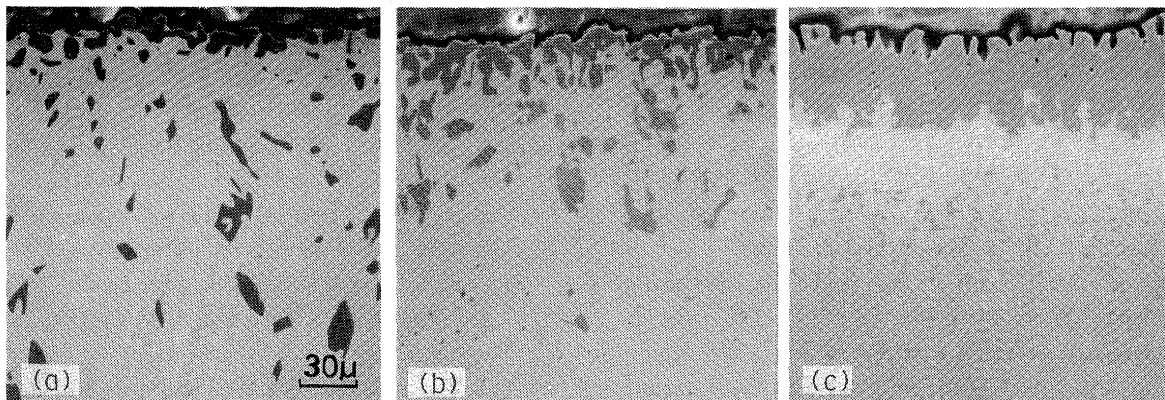


Fig. 17 Crosssectional structure in SEM of Au-Ni alloys after treatment  
(a) Au-5Ni, (b) Au-10Ni, (c) Au-35Ni



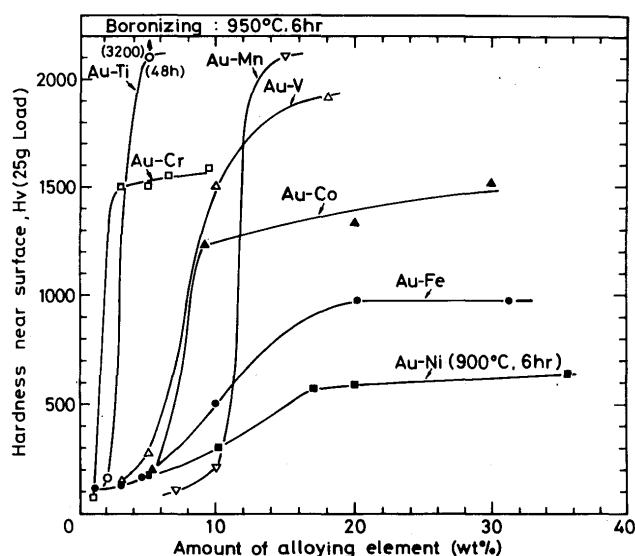


Fig. 18 Effect of amount of alloying element on maximum hardness near surface for various Au-X alloys

For the surface hardening of gold alloy generally one ought to select the alloying element which has a strong potency for hardenability even in a small amount of element, because near pure gold alloy which has a potency of hard surfacing is expectable. For the above purpose the most effective alloying elements for hardening are Cr and Ti within the range of the authors' experiments.

However, on the other side one does not expect excess hardend surface comparing the hardness of base metal. For the above purpose Ni and Fe are preferable.

The maximum hardness for various Au-X alloys shows peculiar value and is not varied with variation of amount of element.

#### 4.3 Marginal temperature for treatment of hardening

Figure 19 shows the effect of treating temperature under the same holding time of 6 hrs on the maximum hardness near surface and the thickness of boride layer for Au-7Cr and Au-35Ni alloys.

Obvious increase in the surface hardness is seen at 900 to 950°C for Au-7Cr and at 800 to 900°C for Au-35Ni alloys, while the thickness of boride layer is gradually increased with an increase in temperature.

#### 4.4 X-ray diffractive analysis of treated surface

Phases detected by X-ray diffraction from the boronized surfaces are collectively tablated in Table 4.

The phase in the first rank, s, for each alloy was prominent intensity. Those in the second, m, and the third, w, were secondary and those in the fourth, vw, were negligible ones. In Au-Ti alloy, for example, Au ( $\alpha$ ) with TiB<sub>2</sub> is detected in case of treatment 950°C, 48 hrs, though TiB<sub>2</sub> is secondary peak due to very thin layer.

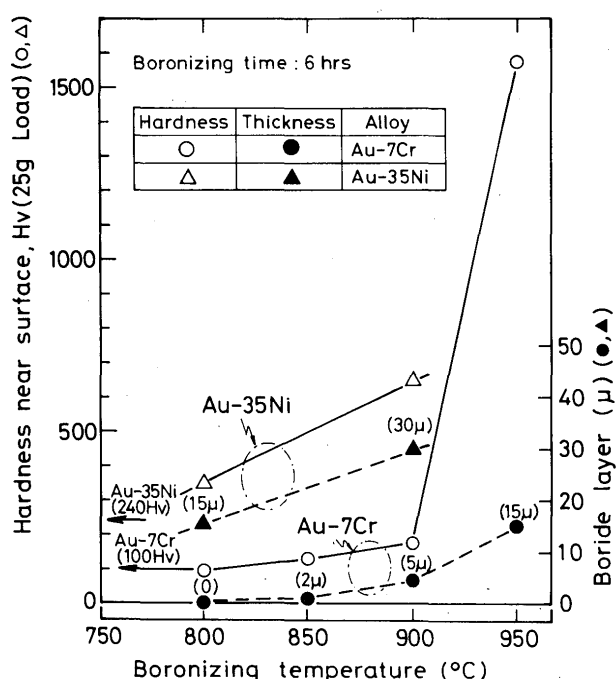


Fig. 19 Effect of boronizing temperature on maximum hardness near surface and thickness of boride layer under the same holding time of 6 hrs for Au-7Cr and Au-35Ni alloys

In general obvious boride of alloying elements predominantly formed when obvious hardening at the surface occurred, while mixture of Au ( $\alpha$ ) and the boride existed in a vague surface for hardening.

#### 5. Conclusions

Surface hardening by means of boronizing with boron powder was experimentally tried to gold alloys containing various amounts of Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, Fe, Co and Ni. The boronizing treatment was done with 950°C, 6 hrs for all gold alloys except Au-Ni alloy of 900°C, 6 hrs and additionally 950°C, 48 hrs for Au-Ti alloy.

As a result the following conclusions were obtained;

- (1) Surface hardening of gold alloys containing Ti, V, Cr, Mn, Fe, Co and Ni was possible by means of boronizing technique which was tried by the authors. The minimum alloying amount in gold required to be hardened was 2 to 5% for Ti, 5 to 10% for V, 1 to 3% for Cr, 10 to 15% for Mn, 5 to 10% for Fe, 5 to 10% for Co and 5 to 10% for Ni. However in case of Au-Ti alloy longer treating time was required for surface hardening compared with other alloys.
- (2) Surface hardening was not obtained for gold alloys containing Zr, Hf, Nb and Ta within the range of this experiment.
- (3) The maximum hardness and the thickness of hardened zone is depended on kind of alloying element after the treatment. Approximately 3200 (Hv) and up

**Table 4** Result of X-ray diffractive analyses of Au-X alloy after boronizing treatment

Alloy (Au-X)	X-ray analysis			
	s*	m*	w*	vw*
Au - 2Ti**	Au(α)	-	-	-
5Ti**	Au(α)	TiB <sub>2</sub>	-	-
Au - 5Zr	Au(α)	-	-	-
Au - 5Hf	Au(α)	-	-	-
Au - 3V	Au(α)	-	-	-
5V	Au(α)	-	-	-
10V	VB <sub>2</sub>	-	-	-
18V	VB <sub>2</sub>	-	-	-
Au - 5Nb	Au(α)	-	-	-
Au - 10Ta	Au(α)	-	-	-
Au - 1Cr	Au(α)	CrB <sub>2</sub>	-	-
3Cr	CrB <sub>2</sub>	Au(α)	CrB	-
5Cr	CrB	CrB <sub>2</sub>	Au(α)	-
7Cr	CrB	CrB <sub>2</sub>	Au(α)	-
10Cr	CrB	Au(α)	-	CrB <sub>2</sub>
Au - 7Mn	Au(α)	-	Mn <sub>2</sub> B	-
10Mn	Au(α)	-	Mn <sub>2</sub> B	MnB
15Mn	MnB	Au(α)	Mn <sub>2</sub> B	-
Au - 1Fe	Au(α)	FeB	-	-
3Fe	Au(α)	FeB	-	-
5Fe	Au(α)	FeB	-	Fe <sub>2</sub> B
10Fe	FeB	Au(α)	-	Fe <sub>2</sub> B
20Fe	FeB	Fe <sub>2</sub> B	-	Au(α)
30Fe	FeB	Fe <sub>2</sub> B	-	Au(α)
Au - 5Co	Au(α)	CoB	-	-
10Co	CoB	Au(α)	-	-
20Co	CoB	Au(α)	-	-
30Co	Co <sub>2</sub> B	CoB	Au(α)	-
Au - 5Ni	Au(α)	Ni <sub>4</sub> B <sub>3</sub>	Ni <sub>2</sub> B	-
10Ni	Ni <sub>2</sub> B	Au(α)	Ni <sub>4</sub> B <sub>3</sub>	-
17Ni	Au(α)	Ni <sub>2</sub> B	-	Ni <sub>3</sub> B
20Ni	Ni <sub>2</sub> B	Ni <sub>3</sub> B	Au(α)	-
35Ni	Ni <sub>2</sub> B	Ni <sub>3</sub> B	Au(α)	-

\* s : very strong or strong  
 m : mediate  
 w : weak  
 vw : very weak

\*\* After 48hrs' treatment

to 10 μm for Au-Ti, 1900 (Hv) and 10 μm for Au-V, 1500 to 1600 (Hv) and 10 to 20 μm for Au-Cr, 2100 (Hv) and 30 μm for Au-Mn, 900 to 1000 (Hv) and up to 80 μm for Au-Fe, 1500 (Hv) and up to 50 μm for Au-Co, 600 to 700 (Hv) and up to 50 to 70 μm for Au-Ni alloys were obtained near the surface.

- (4) From the results of X-ray diffractive analyses for the surfaces after the treatment, the boride layer of alloying element added was detected on the hardened surface, and mixed layer of gold and boride was detected on the nonhardened surface.
- (5) There is some marginal temperature for surface hardening with boronizing treatment for Au-X alloys. In case of Au-Cr and Au-Ni alloys the temperatures are about 900°C and 800°C, respectively.

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