Surface Hardening of Copper-Nickel Alloys with Boronizing[†]

Fukuhisa MATSUDA *, Kazuhiro NAKATA ** and Kenji TOHMOTO ***

Synopsis

By means of boronizing method in argon atmospheric furnace with boron powder surface hardening of various copper-nickel alloy have been investigated. Then the minimum alloying amount of nickel in copper which was required to make surface hardening was determined. Moreover the effects of temperature (700 to 1000°C) and time (up to 6 hrs) dependencies for boronizing were also investigated. As a result, the surface hardening with boronizing layer obviously occurred in the alloys more than 30% nickel in copper when heat treating temperature was raised more than 800°C. However in 5% nickel-copper alloy the boronizing layer without hardening was only seen though in commercially pure copper there was neither boronizing nor hardening layer. The minimum alloying amount of nickel in copper for surface hardening was assumed at about 10%.

The boronized surfaces of these nickel-copper alloys showed about 1000 VHN in maximum hardness and 150 to 200 μm in maximum depth within the range in this investigation, and the precipitation of Ni_2B which was revealed with X-ray diffractive investigation.

KEY WORDS: (Surface Hardening) (Copper-Nickel Alloys) (Boronizing)

1. Introduction

Copper and its alloys are widely used in various industrial fields owing to its effective characteristics such as excellent heat and electric conductivities and good formability and ductility. However softer metal as copper is generally inferior to harder metal in abrasion characteristics. Then hardened copper and copper alloys without any losses of the characteristics of copper have been expected from various industries such as foundry, welding, electricity, machinery etc. Therefore many investigations have been tried for hardening treatments of copper and its alloys such as age-, precipitation and diffusion hardening. Of course surface hardening by diffusion process of special elements has been included in the above investigations.

However there is little information about surface hardening by diffusion process of copper and its alloys within the authors' knowledge.

The authors have investigated in this report about the probability of surface hardening of copper and copper-nickel alloys by means of boronizing process[1] because nickel makes easily hard intermetallic compounds (NiB, Ni_2B etc) with boron and solid solution with copper. The authors wished to know the minimum amount of nickel in copper which causes to make surface hardening, if hardening surface for copper alloy is possible.

Then the effects of nickel amount in copper-nickel alloy on boronizing surface layer such as hardness, thickness and composition have been investigated as variation of boronizing temperature and holding time.

2. Experimental Procedures

2.1 Materials used

(1) Base metal

Copper (Cu) and copper-nickel alloys (Cu-Ni) used in this investigation are shown in **Table 1**. All materials are commercially available and Cu is oxygen-free-copper, 95Cu-5Ni and 70Cu-30Ni are cupronickels, 30Cu-70Ni is monel and Ni is commercially pure nickel.

Specimens of all materials were cut and machined from plates or bars to 10 mm x 10 mm square or 10 mm diam. in 2 mm thickness and the both surfaces were polished by 1500 grade emery papers in advance.

Table 1   Chemical compositions of materials used

Material	Chemical composition (wt %)										
	Cu	Pb	Zn	Fe	Co	P	Mn	C	S	Si	Al	Ni
Cu	99.96	—	—	—	—	—	—	—	—	—	—	—
95Cu5Ni	93.13	0.009	0.02	1.36	0.0017	0.006	0.35	—	—	—	—	5.08
70Cu30Ni	—	—	—	0.64	0.01	—	0.56	0.014	—	0.02	0.01	29.54
30Cu70Ni	33.00	—	—	0.58	0.07	—	0.81	0.117	—	0.17	0.01	—
Ni	—	—	—	—	—	—	—	—	—	—	—	99.96

(2) Boronizing powder

Boronizing powder used is amorphous boron (96.56% B, 0.51% Mg) of 0.1 to 1.0 μm diam..

2.2 Boronizing process

Specimens of all materials were individually filled in boron powder in carbon crucible (25 mm diam.). Then, as shown in **Fig. 1**, the crucible was loaded in an electric furnace for predetermined temperature and time under argon gas flow of 2 l/min.

The temperature of specimen was measured in the bottom of the crucible with a 0.5 mm diam. Pt-PtRh thermocouples.

The boronizing treatments were done under 5 different heating temperatures of 700, 800, 900, 950 and 1000°C and 3 different treating times of 1, 3 and 6 hrs. After boronizing treatment each specimen was investigated for the determination of formation and hardness of boronizing layer metallographically. All hardness tests were done under a 25 g load using Microvickers Hardness Tester.
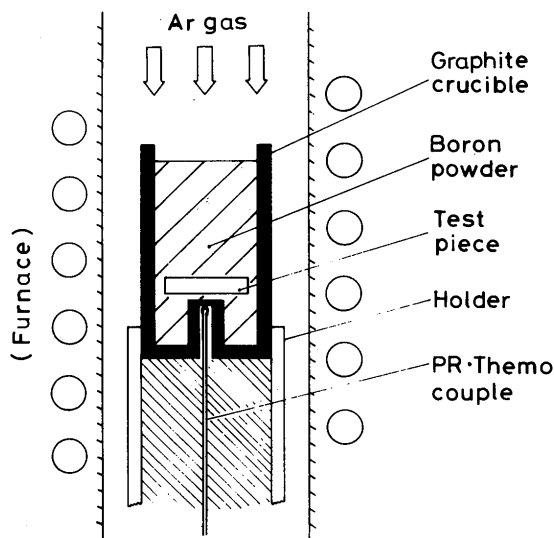

Fig. 1   Test apparatus for boronizing and arrangement of test specimen

3. Experimental Results and Discussions

3.1 Hardness distributions and microscopical observations

(1) Effect of heating temperature

Crosssectional hardness distributions under the surface for each specimen which was treated at 700°C to 1000°C for 6 hrs are shown in **Figs. 2** to **6**. The hardnesses near the surface which are shown in broken lines in **Figs. 5** and **6** show a little reduced values which were due to cracking of hardened surface by indentation of the pyramid cone. There are any hardness changes in pure Cu (OFC) and 95Cu-5Ni even in 1000°C treatment. However in higher nickel alloys more than 70Cu-30Ni alloy the increase in hardness occurs on the surface which was
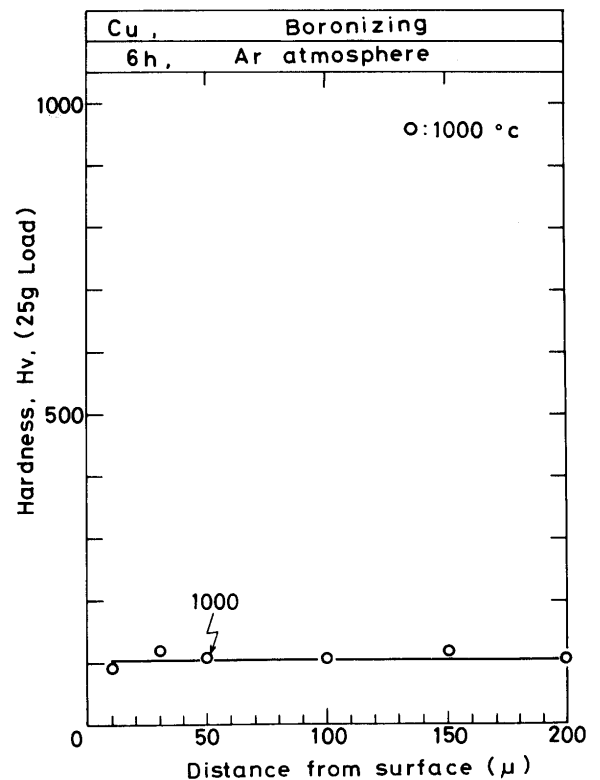

Fig. 2   Crosssectional hardness distribution under the surface of Cu after boronizing at 1000°C for 6 hrs
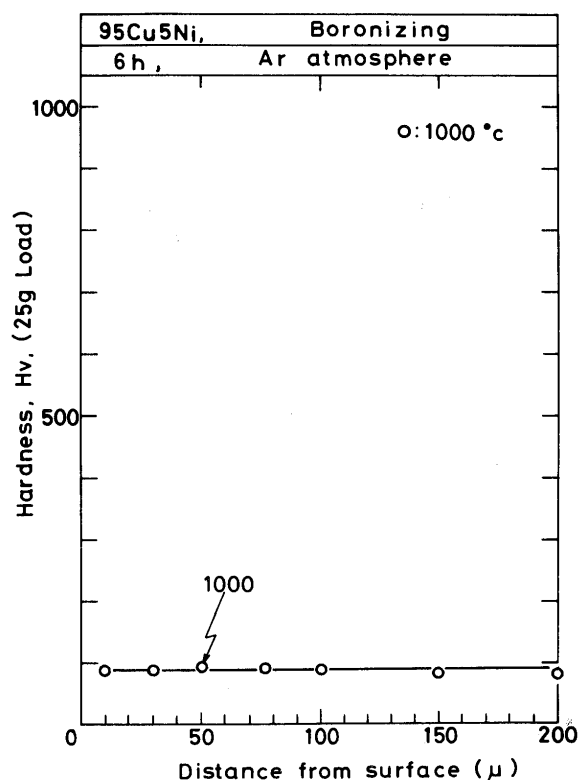
Fig. 3 Crosssectional hardness distribution under the surface of 95Cu5Ni after boronizing at 1000°C for 6 hrs
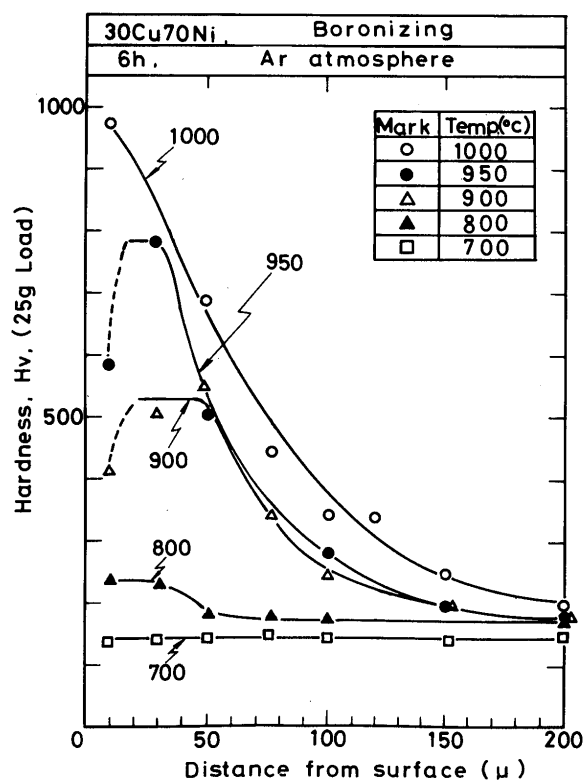

Fig. 5 Effect of temperature on crosssectional hardness distribution under the surface of 30Cu70Ni for 6 hrs' boronizing
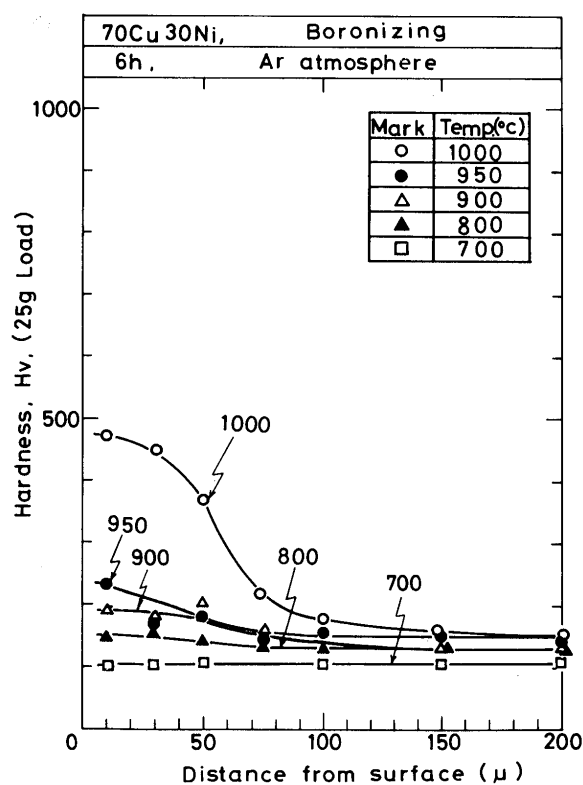

Fig. 4 Effect of temperature on crosssectional hardness distribution under the surface of 70Cu30Ni for 6 hrs' boronizing
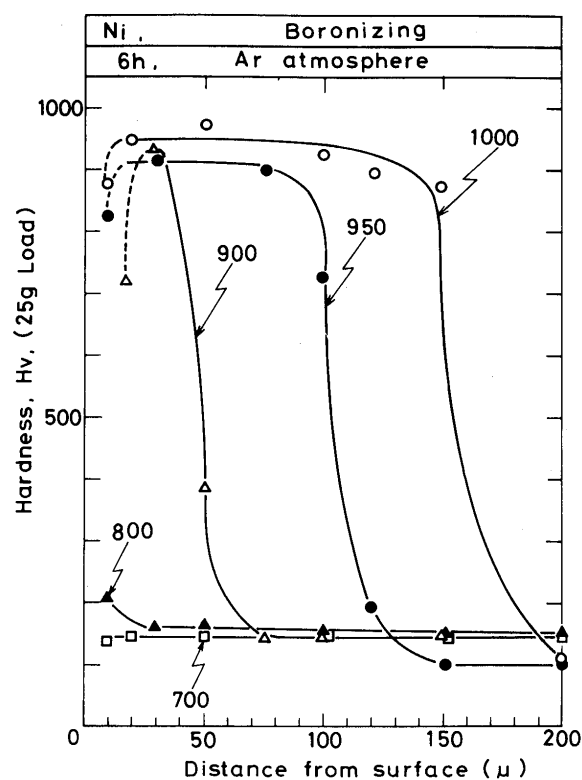

Fig. 6 Effect of temperature on crosssectional hardness distribution under the surface of Ni for 6 hrs' boronizing

treated at temperature more than 800°C. Higher the alloying amount of Ni or the temperature, higher the hardness on surface and thicker the hardened zone.

The maximum hardness appears in pure Ni at about VHN 1000, and the thickness of hardened zone shows in the range of 50 to 200 μm.

Therefore for these alloys the predetermined hardness (up to VHN 1000) and thickness (up to 200 μm) is obtainable in variation of boronizing temperature. The hardness of nickel-boride seems to be about VHN 1000 as shown in Fig. 6.

Figure 7 shows the crosssectional microstructures near surface for various alloys used which were treated at 950°C for 6 hrs.

There is no precipitation in OFC but some precipitations near the surface in 95Cu-5Ni though hardness was not increased.

In 70Cu-30Ni and 30Cu-70Ni alloys the precipitations show a net work pattern near the surface by grown and tied up each other irrespective to the site of grain, though inward the specimen they are preferentially precipitated along grain boundary.

In pure Ni the precipitations clearly make a tight and dense layer of compound on the surface and make needle-like spikings in Ni base metal between compound and base metal. The thickness of the compound layer in Ni metal is rather thinner than the hardened layer of 30Cu-70Ni alloy.

Figure 8 shows the effect of temperature change from 700 to 1000°C under 6 hrs' treatment on the boronizing layer for 30Cu-70Ni alloy. The specimens which were treated more than 800°C showed the precipitation near the surface and with an increase in temperature the density of the precipitation and thickness of the layer were increased. On the surface of 1000°C treated specimen there was partially melted layer, which was caused by
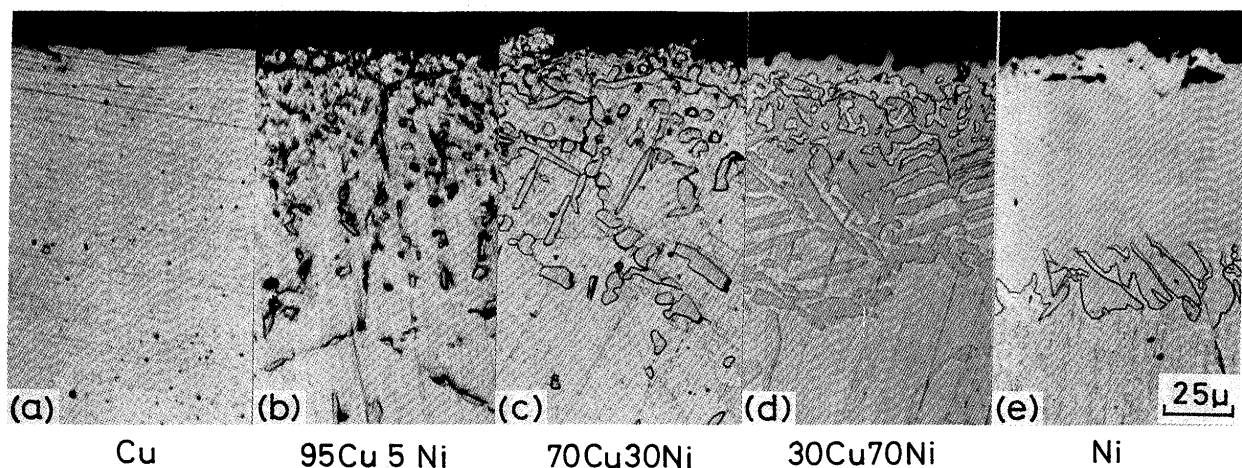

(a) Cu   (b) 95Cu 5 Ni   (c) 70Cu30Ni   (d) 30Cu70Ni   (e) Ni   25μ

Fig. 7   Microstructures of crosssection of Cu, Cu-Ni alloys and Ni after boronizing at 950°C for 6 hrs

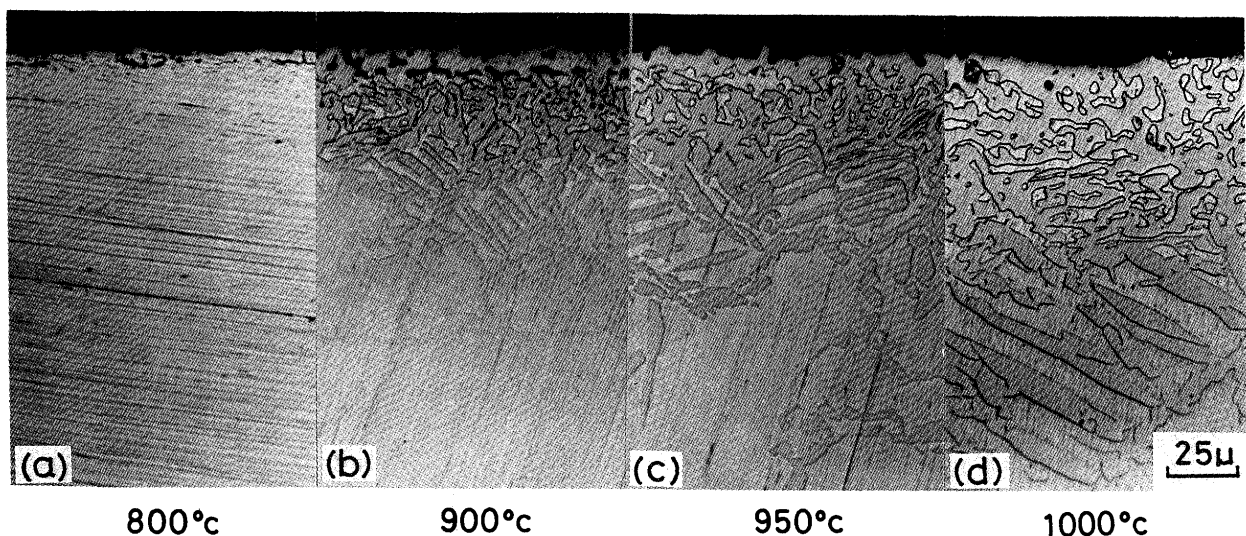(a) 800°c   (b) 900°c   (c) 950°c   (d) 1000°c   25μ

Fig. 8   Effect of boronizing temperature on crosssectional microstructure of 30Cu70Ni for 6 hrs' boronizing time
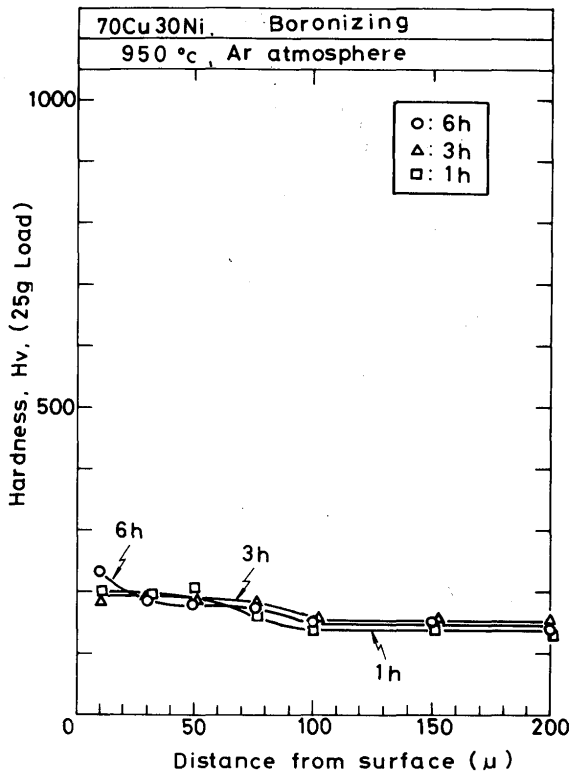
Fig. 9 Effect of boronizing time on crosssectional hardness
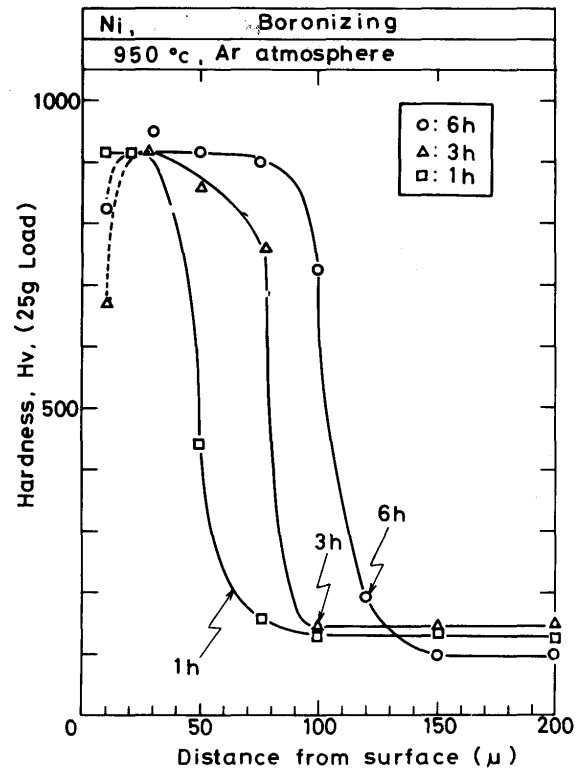distribution under the surface of 70Cu30Ni at 950°C

Fig. 11 Effect of boronizing time on crosssectional hardness
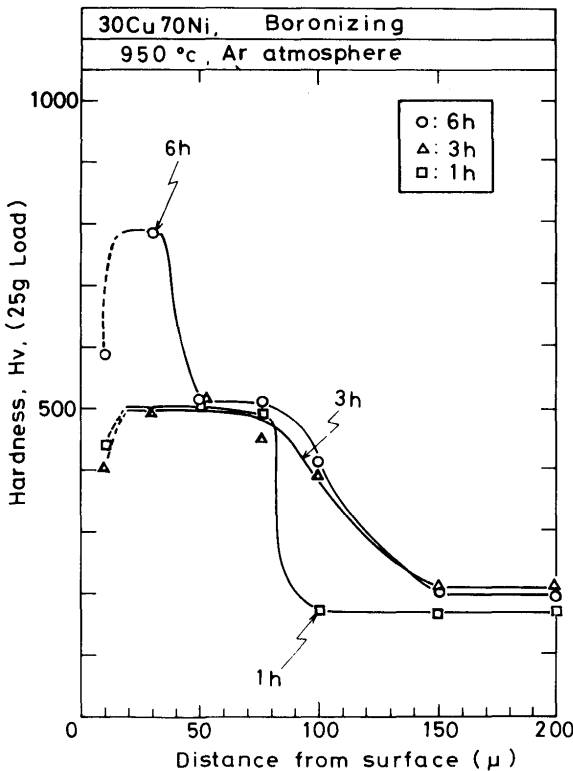distribution under the surface of Ni at 950°C

Fig. 10 Effect of boronizing time on crosssectional hardness
distribution under the surface of 30Cu70Ni at 950°C

a lowering of melting temperature due to formation of Ni-B eutectics which is estimated in Ni-B binary phase diagram[2].

(2) Effect of treating time

In **Figs. 9** to **11** the changes in distribution of cross-sectional hardness are shown for 70Cu-30Ni, 30Cu-70Ni and Ni, respectively, which has been treated for 1, 3 and 6 hrs at 950°C. In 70Cu-30Ni alloy there is no obvious change in hardness although in nickel metal the obvious increase in thickness of hardened layer is seen under the same maximum hardness near the surface.

In 30Cu-70Ni alloy two staged hardness distribution is seen for 6 hrs' treated specimen. The first 30 μm layer on surface side seems to be the same layer as that of Ni.

The effect of treating time at 950°C on hardened layer is microscopically shown in **Fig. 12** for 30Cu-70Ni alloy. Obvious difference in precipitation near surface is not seen between 1 and 3 hrs' treatment but obvious increase in precipitation is seen in 6 hrs' treated specimen, though the thickness in boronizing layer is increased with treating time.

(3) Compositions of boronizing layer

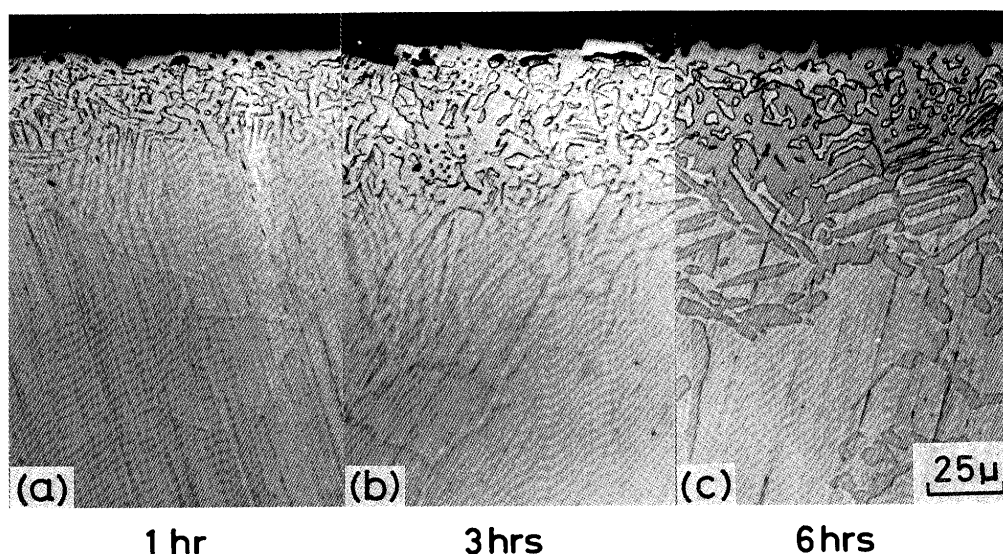X-ray investigation has been done to determine the

Fig. 12 Effect of boronizing time on crosssectional microstructure of 30Cu70Ni at 950°C
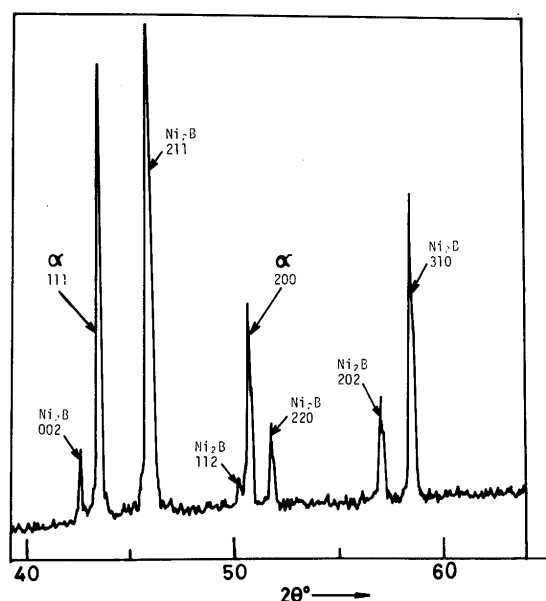

Fig. 13 Typical example of X-ray diffraction pattern from top surface of 30Cu70Ni after boronizing at 950°C for 6 hrs

composition of boronizing surface layer using an x-ray diffractive analyser whose diffractive condition was 35 kv, 15 mA, 4000 cps and copper filter. **Figure 13** shows as an example the result of x-ray investigation for the specimen surface of 30Cu-70Ni which was treated at 950°C for 6 hrs. The peaks of α phase (Cu-Ni solid solution) and Ni_2B are obviously shown in Fig. 13. The same analysing peaks are also seen at the surfaces in other alloys.

However the location of the peaks in α phase shows a little transfer to copper side in comparison with the respective base alloy, which means the reduction of nickel

in solid solution at surface layer due to reaction of Ni in alloy to Ni_2B.

3.2 Discussion on boronizing characteristics

In order to investigate the boronizing process of Cu-Ni alloys the thicknesses of boronizing layer have been measured for the treated specimens under the different conditions of heating temperature and treating time. In **Figs. 14**(a) to (d) the relations between the thickness of layer and square root of time are shown in various temperatures for each alloy. As a result, it is well understood that there are good correlations in those figures between them. Therefore it seems that the formation of the boronizing layer for all alloys used are governed by diffusion process law of boron in Cu-Ni alloy.

That is to say, the following relation is represented $X = Kt^{1/2}$ (X: thickness of boronizing layer (μ), t: boronizing time (hr), K: constant).

Therefore from the results in Fig. 14 Arrhenius plots are shown in **Fig. 15**. The inclination of the lines in Fig. 15 shows activation energy for diffusion of boron in Cu-Ni alloys.

The measured results are shown as 21.0 for 95Cu-5Ni, 25.5 for 70Cu-30Ni and 30Cu-70Ni, and 45.0 Kcal/mol for Ni. Within the authors' knowledge the diffusion characteristics of boron in Cu, Ni or Cu-Ni alloys have not been reported. The activation energy of Be in copper and nickel is reported as 28 (700 to 850°C) and 46.2 (temperature is not known) Kcal/mol, respectively[3].
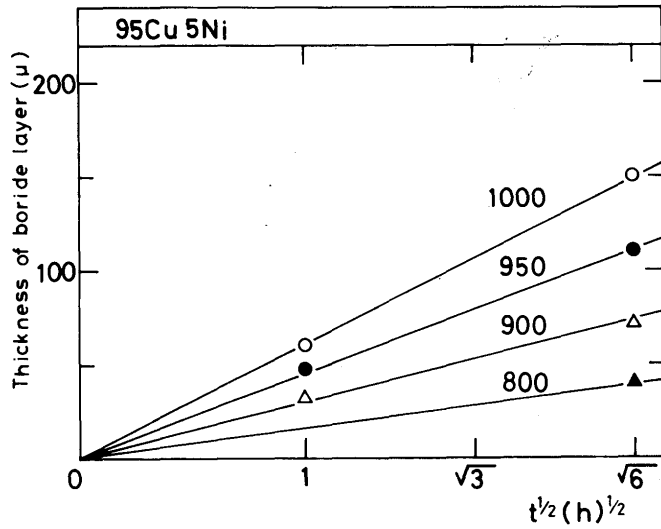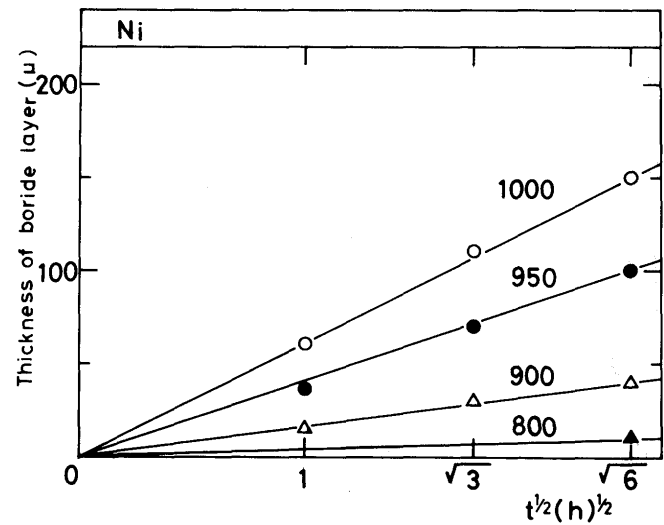
(a) 95Cu5Ni
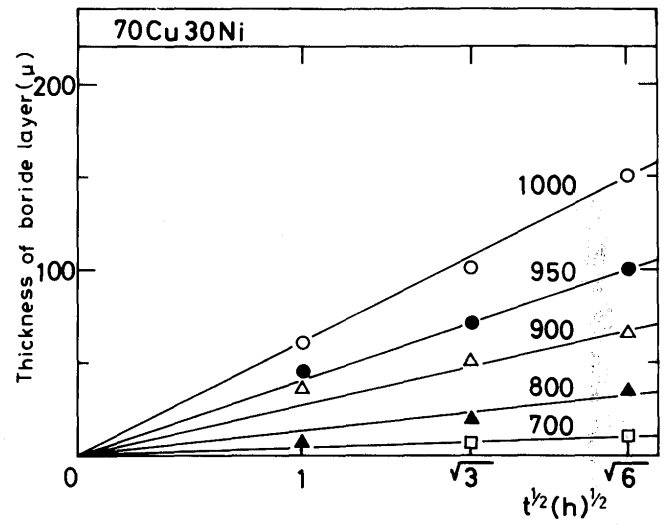
(b) 70Cu30Ni
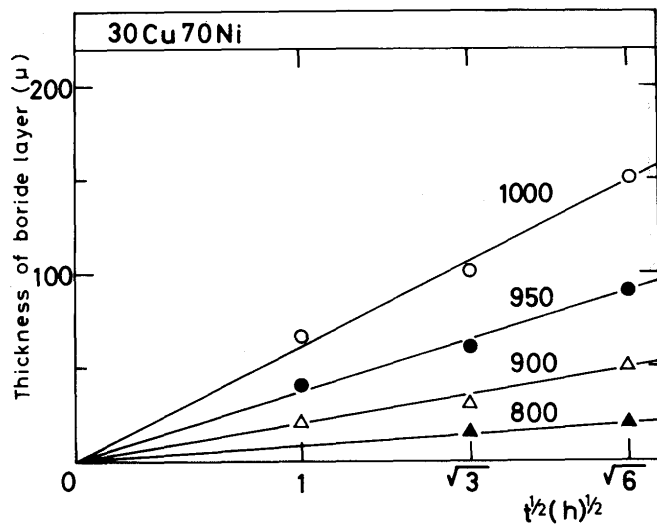
(c) 30Cu70Ni

(d) Ni

Fig. 14 Thickness of boronizing layer vs. square root of boronizing time under various boronizing temperatures
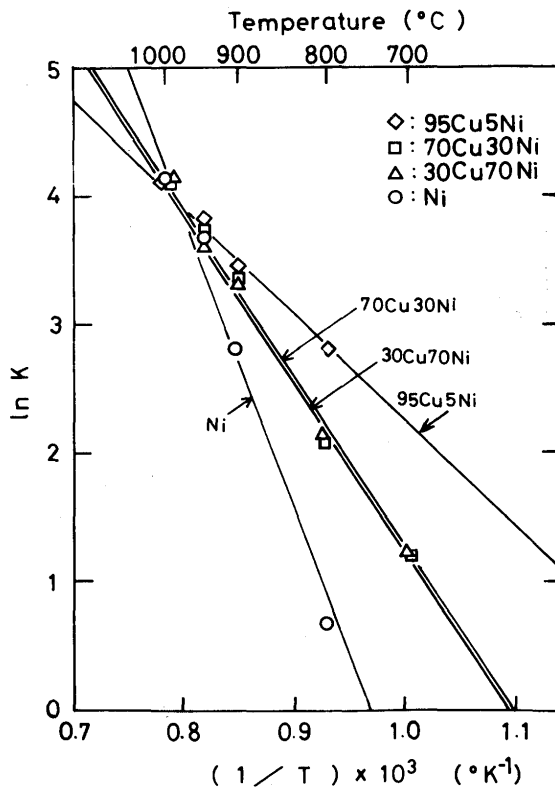
Fig. 15 Arrhenius plot of velocity constant for boronizing

is more than 800°C. The maximum hardness and the thickness of hardened zone in this experiment strongly depend on boronizing temperature, time and content of nickel, and those values are in the range of VHN 500 to 1000 and less than 200 μm. In copper-5% nickel alloy the precipitation of $Ni_2 B$ in alloy was observed near surface of the specimen but the hardness was not increased, and in commercial pure copper there was no precipitation and hardening phenomena on surface.

(2) In commercial nickel the maximum hardness on specimen surface showed VHN 900 to 1000 and the thickness of the hardened zone was changed with increases in temperature and time. There was no surface hardening even in nickel when boronizing treatment under 700°C was done.

(3) According to X-ray diffractive investigation the cause of increase in surface hardness was due to formation of $Ni_2 B$.

(4) Thickness of the boronizing zone was increased with an increase of square root of time for treatment at constant temperature. The activiation energy for diffusion of boron in each alloy was estimated from this investigation.

4. Conclusions

Using a boronizing process the surface hardening of copper metal, copper-nickel alloys and nickel metal has been investigated.

Effect of treating temperature (700 to 1000°C), treating hours (max. 6 hrs) and nickel content in copper-nickel alloy on the hardness and thickness of the hardened zone has been mainly studied.

The conclusions obtained are as follows;

(1) The copper-nickel alloys whose Ni content is more than 30% show obvious increase in surface hardness by the boronizing process whose treating temperature

Acknowledgements

References

1) M. Kawakami; NETSU SHORI, 10 (1970) 4, 266-269. (in Japanese).

2) M.E. Shunk: "Const. of binary alloys, second supplement" (1969).

3) The Japan Institute of metals; Metals Data book (1974), p. 25 (in Japanese).