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Surface Hardening of Silver Alloy with Boronizing Technique†

Fukuhisa MATSUDA*, Kazuhiro NAKATA** and Masaki MORIKAWA***

Abstract

The feasibility of hardfacing of silver alloy with boronizing technique using pure boron powder was investigated. As a favorable alloying element to have a good affinity with boron and good solubility in silver, only manganese was selected to satisfy the above condition among IVa, Va, VIa, VIIa and VIII group metals in the Periodic Table. Surface hardening with boronizing technique was possible for Ag-5, 10, 15, 20 and 25%Mn alloys, and maximum hardness and thickness of hardened zone were Hv 700 to 1200 and 15 to 35 μm at the treating temperature of 1173K for 21.6 ks. These hardened zones composed of the outer MnB boride phase and inner Mn₂B boride phase. Moreover the spiky Mn₂B phase had a strong coalescence with substrate base metal.

KEY WORDS: (Hardfacing) (Surface Hardening) (Boronizing) (Boriding) (Silver) (Silver Alloy) (Manganese)

1. Introduction

It is very important to provide the hard surface layer on industrial materials to protect them from abrasion, erosion and so on. Therefore there are so many works about hardfacing of industrial materials. It is, however, interesting that there are few reports, within the authors' knowledges, about hardfacing of nonferrous metals and alloys in contrast with ferrous materials.

Therefore the authors have started a research program about surface hardening of nonferrous metals and alloys by surface diffusion process of small-sized atoms such as nitrogen, boron and carbon.

At the first step as shown in the previous report¹⁻²⁾, the feasibility of surface hardening of various pure metals was examined to select easy metal for the hardfacing from them by means of ion-nitriding process¹⁾ and boronizing process²⁾. As a result, in the Periodic Table most of IVa, Va, VIa, VIIa and VIII group metals and their alloys were feasible to surface hardening with either ion-nitriding or boronizing processes, except that cobalt and nickel in VIII group metal were unfeasible with ion-nitriding process. On the contrary, it was unfeasible on Ib group metals (copper, silver, gold) and IIIb group metal (Al) by means of neither ion-nitriding nor boronizing processes.

At the second step, the authors have introduced a new concept for hardfacing of these Ib group metals with boronizing technique, that is, when some alloying ele-

ments which have a strong affinity with boron are added in Ib pure metal such as gold, boron atoms diffused into gold alloy with boronizing process are contact with alloying atoms and subsequently hard boride precipitates on its surface layer. The applicability of this new hardfacing process assisted with boronizing technique to Ib group metals was ascertained on gold binary alloys²⁾ containing titanium, vanadium, chromium, manganese, iron, cobalt or nickel and copper-nickel alloys³⁾.

In this report, the same procedure was adopted on silver alloy to confirm the feasibility of surface hardening with boronizing process and find out some adequate alloying elements to silver metal and their marginal amount for surface hardening.

Then, hardness measurement, microstructural observation by optical microscope and scanning electron microscope (SEM) with EDX analyzer and X-ray diffractometry of boronized layer were performed.

2. Experimental Procedures

2.1 Materials used

As a suitable alloying element to silver, next two conditions should be satisfied; one is the strong affinity with boron and other is enough solubility to silver.

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As already mentioned in the previous report²⁾, IVa, Va, VIa, VIIa and VIII group metals in the Periodic Table have the strong affinity with boron. The solubility of these metals to silver was examined from equilibrium silver binary phase diagram⁴⁾. Alloying elements were divided roughly into 5 groups depending on the solubility range in silver at 1073 – 1173K as shown in Table 1.

Table 1 Solubility of alloying elements in silver at 1073 to 1173K from silver-rich binary phase diagram⁴⁾

Solubility range (1073-1173K)	Alloying element	Amount of solubility (wt%) (1073-1173K)
100%	Au Cu Pd Pt	100
More than 10%	Mn	21 - 25
1 - 10%	Al Mg	1.5 - 4.5 1.6 - 6.0
Less than 1%	Be Ti (Y) (Sm)	0.13 - 0.3 0.5 - 1.0 0.1 at 1048K 1.0 at 1048K
No solubility	Ce La Zr	Two melts
	Cr Ni U	
	Co Fe V	Insoluble in liquid

Among them, manganese is only element to have a strong affinity with boron and good solubility up to 25%. Chromium, cobalt, nickel, iron and vanadium have no solubility in silver and titanium has only 1% of solubility, and moreover these elements are very difficult to be alloyed in silver in spite of their strong affinity with boron.

Consequently, according to these preliminary considerations, Ag-Mn binary alloy was selected in this study to be possible one for surface hardening with boronizing.

Button-like ingots of about 20g of Ag-5, 10, 15, 20 and 25%Mn binary alloys were made by vacuum-purged tungsten-arc in argon atmosphere from commercial 99.99% Ag shots and 99.9%Mn. Buttons were remelted three times overturning it upside down for each remelting to get good mixture between silver and manganese and subsequently they were hot-rolled in stainless sheath to 1 mm thick sheet and annealed at 1073K. Manganese contents of these alloys chemically-analyzed were as shown in Table 2.

2.2 Boronizing technique

The same boronizing technique as utilized in the previous report²⁾ "boron powder pack process" was employed using a commercial amorphous boron powder (96.6% boron, 0.1 – 1.0 μm diameter).

Test specimen, 10x10x1 mm thickness, was polished

Table 2 Results of chemical analysis of Ag-Mn binary alloys made

Alloy	Nominal Composition (wt%)	Chemical Composition (wt%)
Ag- 5Mn	5	4.69
-10Mn	10	10.60
-15Mn	15	14.44
-20Mn	20	19.37
-25Mn	25	24.68

with #1500 emery paper and rinsed with acetone, and then packed into boron powder in carbon crucible (25 mm diameter). Heat treatment was performed at 973 to 1173K for 3.6 ks (1hr) to 21.6 ks (6hr) with electrically heated furnace under a shielding flow (0.03 lit./sec) (2 (lit./min) of argon gas.

After boronizing treatment, the crosssection of the treated specimen was polished, and then vickers hardness measurement with 0.25N (25g) load and microstructural investigation of optical microscope and scanning electron microscope (SEM) were done. Element distributions of Ag, Mn and B in boronized layer were also examined with EPMA. Moreover, the identification of boride formed was carried out with X-ray diffractometry by using Cr-Kα radiation (40kV, 20mA) on the boronized specimen surface.

3. Experimental Results and Discussions

3.1 Effect of manganese content on hardness of boride layer

As expected, obvious boride layer was formed on the surface of Ag-Mn binary alloys with more than 5%Mn content with boronizing treatment at 1173K for 21.6ks. Figure 1 shows the hardness and thickness of boride layer measured on crosssection of treated specimens as a function of manganese content in silver.

The hardness of boride layer (broken line in Fig. 1) which was considerably scattered was much higher than those of base metal alloys (Hv 36–53 in 5–20%Mn and Hv 110 in 25%Mn) and increased as the increase of Mn content from Hv 280–680 in 5%Mn to Hv 550–1170 in 25%Mn, though the most probably hardness value was almost saturated to about Hv 700 with more than 10%Mn content.

The thickness of boride layer increased as the increase in Mn content from approximately 15 μm in 5%Mn to 35 μm in 25%Mn, but with more than 10%Mn, the increase in the boride-layer thickness became small.

Therefore the marginal amount of Mn content in silver to realize the hardfacing with boronizing process was 5% within the range in this experiment.

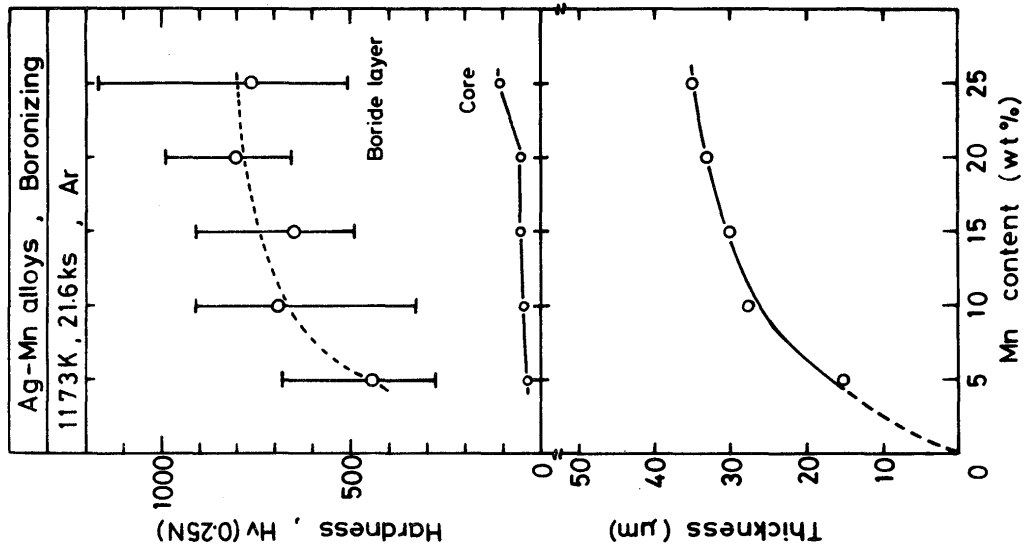


Fig. 1 Effect of manganese content in silver on hardness and thickness of boride layer (1173K, 21.6ks)

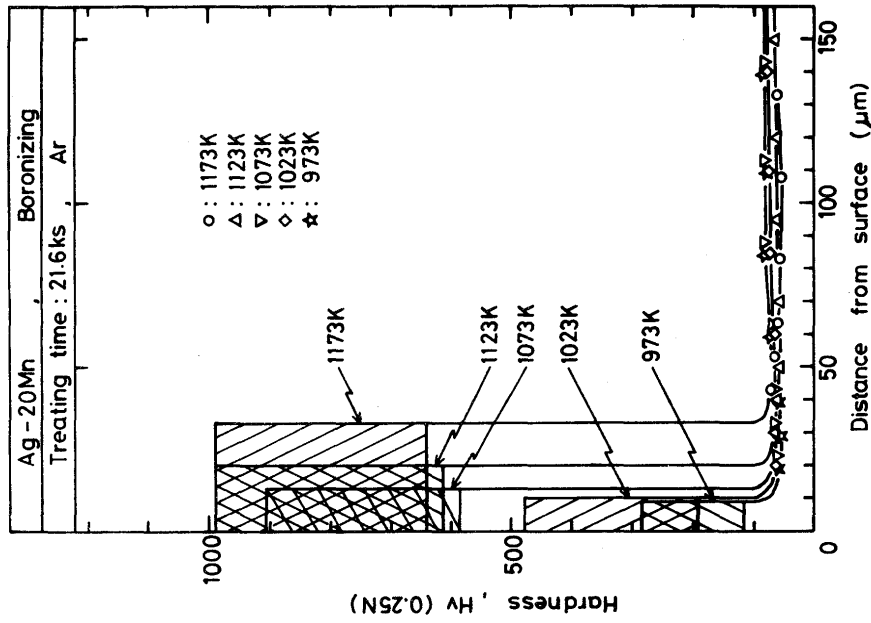


Fig. 2 Crosssectional hardness profiles of Ag-20%Mn alloy at different treating temperature for 21.6ks

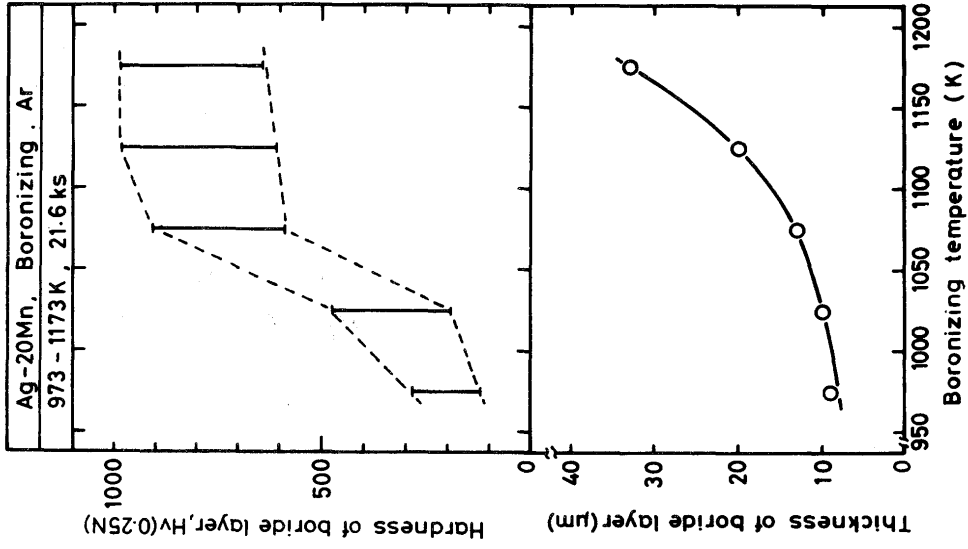


Fig. 3 Effect of treating temperature on hardness and thickness of boride layer of Ag-20%Mn alloy for 21.6ks' treatment

3.2 Effect of boronizing condition on hardness and thickness of boride layer

Hardness distributions on crosssection of Ag-20%Mn alloy are shown in Fig. 2 and the hardness and thickness of boride layer are also shown in Fig. 3 against the variation in treating temperature from 973 to 1173K under the constant treating time of 21.6ks.

Hardness of boride layer increased as the increase in treating temperature from 973 to 1073k, but it was almost saturated to the hardness range Hv 600 – 1000 at higher temperature than 1073K and in this temperature range boride thickness was much increased as the rise in treating temperature.

Nextly, Figure 4 shows the effect of boronizing time on hardness of boride layer measured on crosssection of Ag-20%Mn alloy treated at 1173K up to 21.6ks. This figure indicates that when the dense boride layer is formed, its hardness approximately Hv 990 in maximum, is not varied by treating time at longer than 3.6ks, though the hardness was slightly lower at 1.8ks' treating time. The same tendency was observed on boronized pure nickel³⁾.

On the contrary, thickness of boride layer was much influenced with treating time as shown in Fig. 5 which shows the relation between boride thickness and treating time for Ag-20%Mn alloy at different treating temperature. Boride layer grew as a following parabolic growth rate law for each treating temperature; $X = k_p t^{1/2}$, where X: boride layer thickness, k_p : parabolic growth rate constant, t: boronizing time.

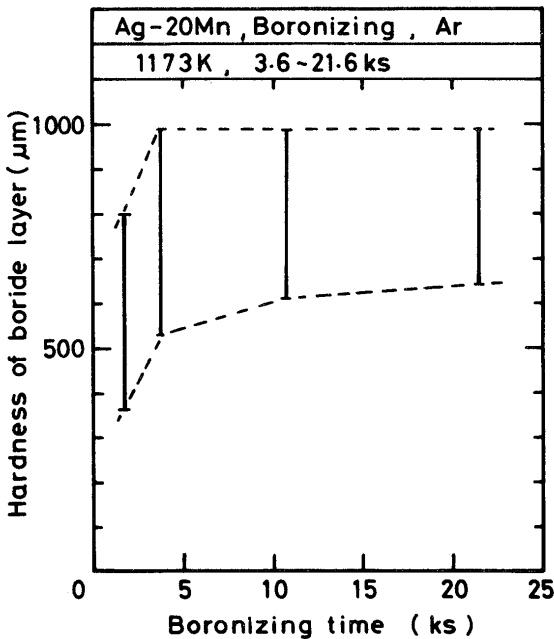


Fig. 4 Effect of treating time on hardness of boride layer of Ag-20%Mn alloy treated at 1173K up to 21.6ks

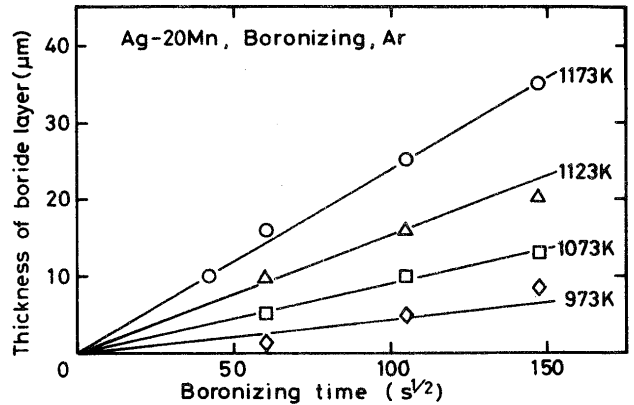


Fig. 5 Relation between thickness of boride layer and treating time for Ag-20%Mn alloy treated at different temperature (973 to 1173K)

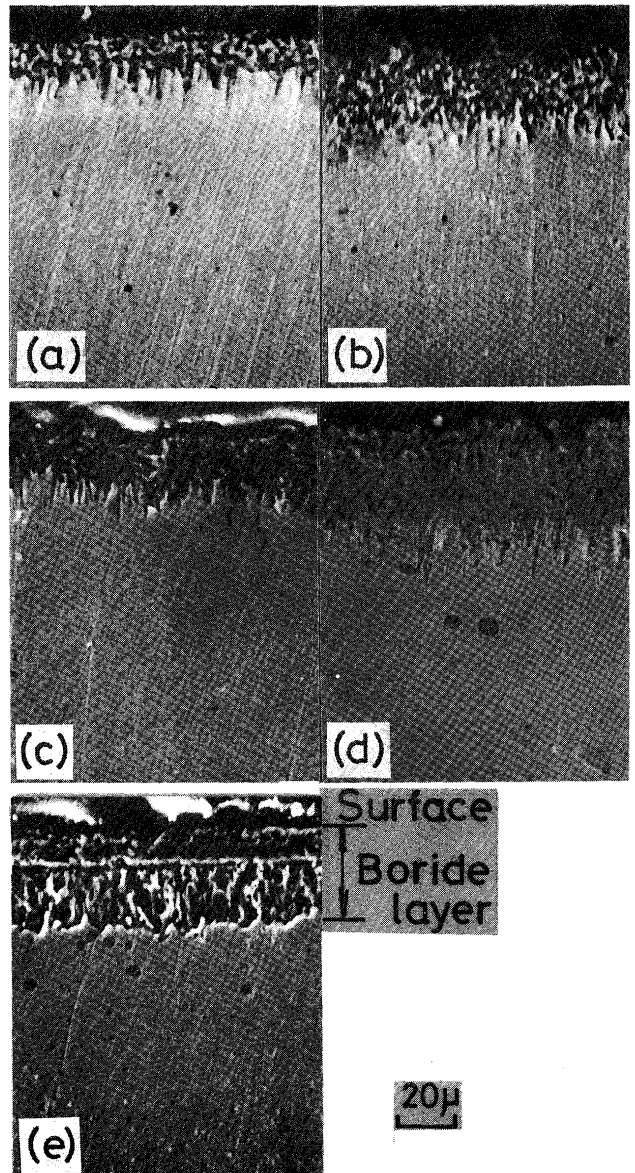


Fig. 6 Crosssectional microstructures of boride layer treated at 1173K for 21.6ks: (a) Ag-5%Mn, (b) Ag-10%Mn, (c) Ag-15%Mn, (d) Ag-20%Mn, (e) Ag-25%Mn

3.3 Microstructure of boronized zone

Figure 6 (a), (b), (c), (d) and (e) shows the cross-sectional microstructures of boride layer treated at 1173K for 21.6ks for Ag-5, 10, 15, 20 and 25%Mn alloys, respectively.

When the Mn content in Ag alloy was as small as 5 and 10%, boride layer almost consisted of one flat layer, though needle-like phase was sometimes observed at the interface between surface boride layer and substrate base metal.

On the contrary, at more Mn content than 15%, boride layer obviously consisted of two layers, which were outer flat layer and inner spiky layer as shown in (c) and (d), though on 25%Mn alloys as shown in (e), the spiky interface became comparably smooth. This means that the precipitation density of needle-like phase below outer layer

was increased as the increase in Mn content in silver alloy.

Effect of treating temperature on cross-sectional microstructure is shown in Fig. 7 (a), (b), (c), (d) and (e) at treating temperature of 973, 1023, 1073, 1123 and 1173K, respectively for Ag-20%Mn alloy for 21.6ks' treating time. Boride layer consisted of two layers at each temperature, but flat interface between inner boride layer and substrate was observed below 1173K and the spiky interface was only observed at 1173K as shown in Fig. 7 (e).

From these figures in Figs. 6 and 7, there are many small voids in boride layers. This seems to be one of the reason of comparably large scattering in hardness of boride layer, though the mechanism of this void formation was not clear in this study.

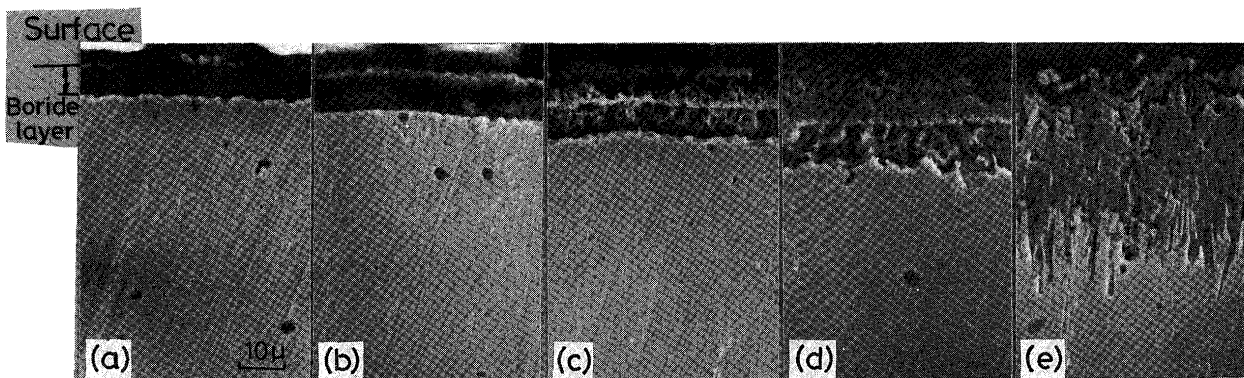


Fig. 7 Cross-sectional microstructures of boride layer of Ag-20% Mn alloy at different treating temperature for 21.6ks: (a) 973k, (b) 1023K, (c) 1073K, (d) 1123K, (e) 1173K

3.4 Composition of boride layer

Figure 8 shows the distribution of Ag, Mn and B measured with EPMA through boronized zone on cross-section of Ag-20%Mn alloy treated at 1173K for 21.6ks.

Much build-up of boron together with manganese but almost non of silver in boride layer was observed. Boron content in outer boride layer was much more than that in the inner one. Moreover, denude zone of manganese in substrate base metal below the boride layer was clearly observed. However, boron penetration into substrate base metal was not clear.

In order to identify the boride layer, X-ray diffractive analysis was carried out for the boronized specimens treated at 1173K for 21.6ks. Typical X-ray diffractive pattern against 20 degree are shown in Fig. 9 (a), (b) and (c) for Ag-5, 15 and 25%Mn alloys, respectively.

Only MnB as boride phase was clearly detected together with silver from substrate base metal up to 15%Mn content and the relative intensity of MnB against Ag(α) increased as the increase in Mn content. Two boride phases

Mn₂B and MnB were detected with more than 20%Mn content together with very weak Ag(α) peak and relative intensity of Mn₂B against MnB increased as the increase in Mn content. According to microstructural and X-ray diffractive analyses, it is decided that outer flat boride layer consists of MnB phase and inner spiky layer consists of Mn₂B phase.

In case of Ag-5, 10 and 15%Mn alloys, Mn₂B was precipitated as a very thin needle-like phase between the outer dense MnB layer and substrate base metal and moreover its precipitation amount was a little. On the contrary, in Ag-20 and 25%Mn alloys Mn₂B phase precipitated as the dense thick layer. Therefore this seems to be the reason why the Mn₂B phase was not detected in Ag-5, 10 and 15%Mn alloys by X-ray diffraction analysis on boronized specimen surface.

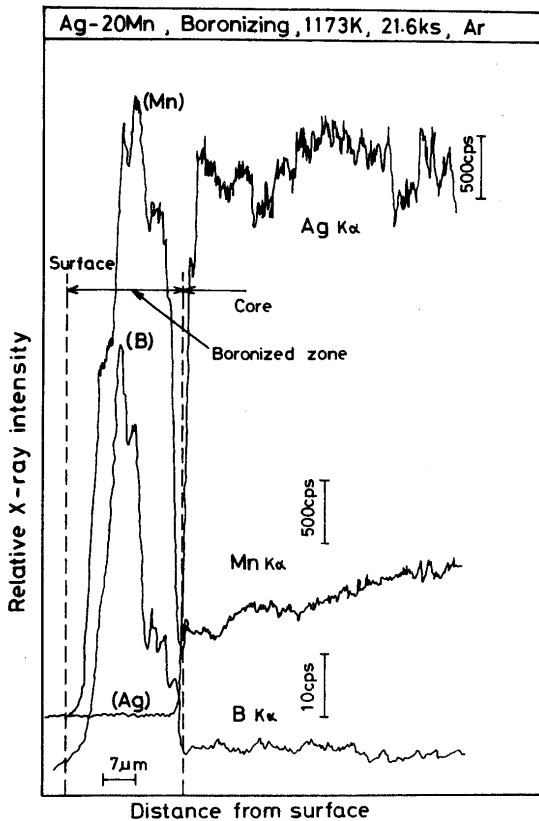


Fig. 8 Distribution of silver, manganese and boron elements through boronized zone of Ag-20%Mn alloy treated at 1173K for 21.6ks

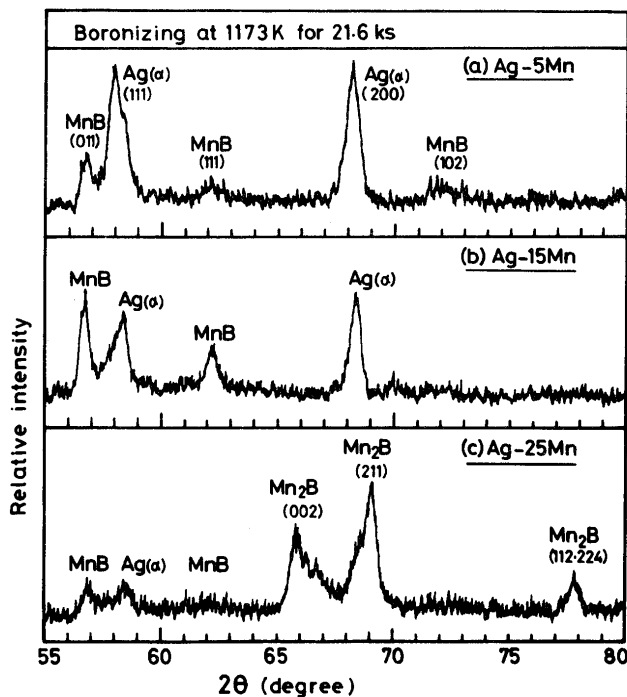


Fig. 9 Typical X-ray diffractive pattern obtained from surface of boronized Ag-Mn alloys treated at 1173K for 21.6ks (Cr - K α radiation)

3.5 "Peel-off" phenomena of boride layer

In this paper, no testing about the mechanical properties was carried out except for hardness measurement because of a small-sized specimen.

However, "peel-off" phenomena of a part of boride layer was sometimes observed on the crosssections of boronized specimens. "Peel-off" of boride layer occurred mainly at the interface between outer MnB and inner spiky Mn₂B, and it was rarely observed at the interface between spiky Mn₂B and substrate base metal. This means because the spiky phase penetrated into base metal acts such as the anchor which connect the boride phase tightly with substrate base metal.

Therefore, as to the resistant to "peel-off" of boride layer, the spiky Mn₂B phase is a favorable one.

4. Conclusions

The feasibility of surface hardening of silver alloy containing manganese up to 25% has been investigated with boronizing technique by using a powder boron-pack-process. Main conclusive remarks obtained in this study are as follows;

- 1) Only manganese was a favorable alloying element to silver to enable the surface hardening with boronizing technique, because manganese had a strong affinity with boron and good solubility in silver.
- 2) Obvious surface hardening has been observed on Ag-5, 10, 15, 20 and 25%Mn alloys at the treating temperature of 973 to 1173K. Maximum hardness and thickness of hardened layer were Hv 700 to 1200 and 15 to 35 μ m at 1173k for 21.6ks respectively, though there was considerable scattering in hardness.
- 3) Hardened layer consisted of two boride phases, that is, outer MnB and inner Mn₂B layers. As an increase in Mn content in silver alloy, the precipitation of Mn₂B became more dense.
- 4) Inner Mn₂B phase was inclined to grow making a spiky interface in the substrate base metal. This seems to have a strong coalescence with substrate base metal.

Acknowledgements

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