

Surface Treatment of Steel by Plasma Boronizing

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Abstract

At present the processes of boronizing have been mostly studied in a plasma from gaseous compounds containing the impregnating element and are in an industrial use. These have been investigated by a variety of works in a glow discharge with different mixture ratios of B_2H_6 and H_2 as well as BCl_3 and H_2 . The active atmosphere has been diluted by Ar or some other inert gas in order to enhance control of boron potential and to reduce the ignition voltage of the glow discharge. The Control of gaseous atmosphere is essential to a boride layer in plasma boronizing treatment. The boride formation is required to make the workpiece surface saturated with boron content. The present study considers the efficiency of plasma boronizing reactions and the morphology of boride layer under various plasma conditions

1. Introduction

The surface hardening process such as nitriding, carburizing and boronizing are well established as thermochemical diffusion processes. These processes are widely used in the manufacturing and machinig industries primarily to treat engine components, tools for hot or cold work, die castings, machine tools and tribocomponents. These processes are based on diffusion of the nonmetallic interstitial elements, nitrogen, carbon or boron, into the surfaces. Nitrogen diffusion in steels is usually performed in the ferrite phase between $450^\circ C$ to $600^\circ C$, whereas carbon and boron diffusion is performed in the austenite phase between $750^\circ C$ to $1000^\circ C$.

These processes can be divided into two broad categories which are conventional and plasma assisted processes. The conventional case hardening processes are performed in solid, liquid or gaseous mass transfer media. Plasma assisted processes are based on the energetic nature of the glow discharge. The high energy of the plasma contains ions, electrons, radicals

and activated species. The use of the plasma offers great flexibility in tailoring surface properties independent of the bulk properties when the treatment variables are properly controlled.

The plasma nitriding and carburizing processes have gained wide industrial acceptance primarily for increasing wear resistance and antigalling and improving fatigue life and corrosion resistance. However, the more recently introduced plasma boronizing process stands on the edge of industrial applications.

Plasma boronizing is a process which makes it possible to produce a layer of borides on the surface of steel. Such borides have good working properties, e.g. hardness and wear resistance, as well as considerable resistance to many chemical reagents. The technical and economic advantages of plasma heat treatment as revealed in the nitriding process, namely a low energy and gas consumption and the possibility of controlling the phase composition of diffusion layers, have been extended in the case of boriding through a reduction of the treatment time and a lowering of the treatment temperature as compared with the conventional process[1-3]. The plasma boronizing process involves the treatment of a material in the presence of an ionized and dissociated molecular gas. The workpiece is gently bombarded with active ionized gases and is heated to the desired temperature to permit their diffusion into the surface. The change in chemical composition of the surface produces the hardened boride layer. Since the availability of the active ionized gas is determined by the discharge and does not depend on the catalytic response of material surface, the plasma process has greater flexibility to establish the concentrations of elements to be diffused into the surface and the temperature of the material required to sustain the desired diffusion rates. Thus one should expect improvements in the temperature which could translate to a general economic advantage over conventional processing

2. Experimental Procedure

The materials chemical compositions used in this investigation are shown in Table 1. The samples were finished to less than $0.3\mu\text{m}$ surface finish by conventional grinding and polishing prior to treatment.

The samples were boronized by the plasma boronizing system shown in Fig. 1. The plasma boronizing process involves introducing the samples to be treated into a reaction chamber where it serves as the cathode.

The reactive gas, namely a mixture of BCl_3 vapours and H_2 , is introduced

into the reaction chamber under a pressure of 5 to 30 mbar where upon a potential difference between the cathode and anode of up to 500V was applied. The details of the plasma boronizing condition, are shown in Table 2. The boronized surfaces were characterized by microvickers hardness test, X-ray diffraction, SEM and optical microscopy. Hardness depth profile and microstructure were performed on cross-section samples.

Table 1. Chemical composition of test samples

Material \ Composition	C	Cr	Cu	Mn	Mo	Ni	V	Fe
SS41	0.40	-	-	0.70	-	-	-	Rest
SNCM8	0.40	0.74	0.28	0.68	0.25	1.87	-	Rest
STD61	0.40	5.25	1.00	-	1.25	-	1.05	Rest

Table 2. Experimental Conditions

Initial Vacuum	1×10^{-2} mbar
Working Pressure	5 ~ 30 mbar
Gas Mixture	H ₂ : Ar = 50vol% : 50vol%
Amount of BCl ₃	0.1vol% ~ 0.5vol%
Boronizing Temp.	750°C ~ 850°C
Boronizing Time	1hr ~ 4hr

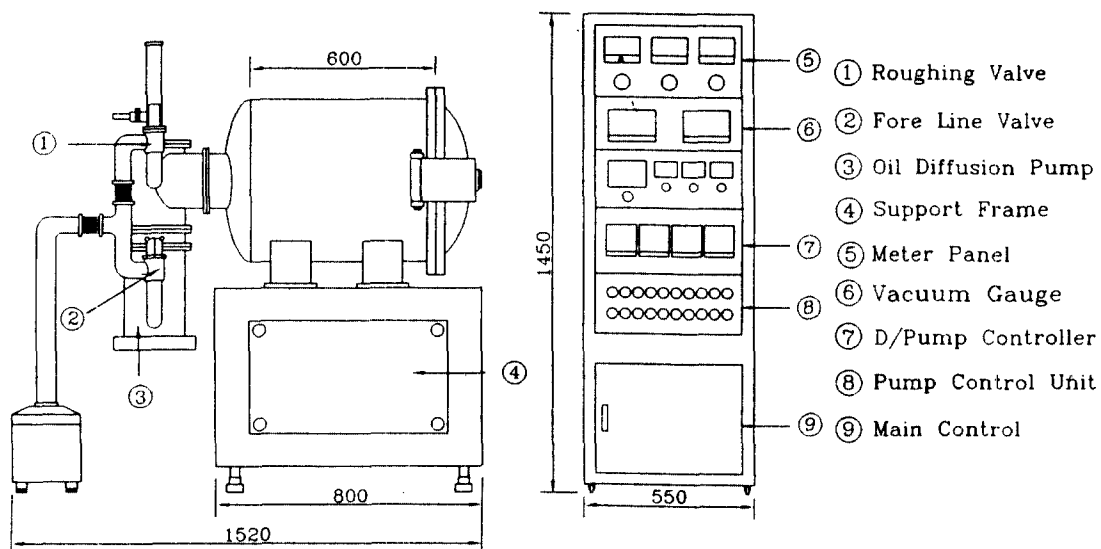


Fig.1 Schematic diagram of the plasma boronizing system

3. Results and Discussion

Presently there is no universal model which explains the plasma boronizing process. However numerous mechanisms have been proposed to explain this concept. The fact remains that the exact reactant species in the glow discharge during plasma boronizing are not well identified. Basically the plasma boronizing process is controlled by plasma mass transfer and plasma surface interactions. All the proposed mechanisms are essentially derived from this basic contributing factors.

- ① Sputtering
- ② Ion excited atom implantation
- ③ Adsorption, and
- ④ Condensation / deposition

In plasma boronizing, the presently proposed mechanism is by B transfer from the BCl_3/H_2 plasma to the specimen through the dissociation of BCl_3 within the glow and forced attraction of the boron species to the specimen(cathode) and finally reaction at the surface. The microstructure and the growth rate of the boride layer are influenced by the treatment temperature, the gas mixture and the material composition.

In this study, only three process variables(temperature, gas mixture ratio, and treatment time) have been controlled to optimize the microstructure, thickness, and microhardness of boride layer. The variation of boride layer as a function of treatment temperature on SS41, SNCM8, and STD61 are given in Fig.2. Between 750 and 850°C, and for a treatment time of 4hr the boride thickness on SS41 increased up to 15 μm ~ 20 μm . The growth rate of the boride layer of SS41 is higher than of SNCM8 or STD61. This is caused by the higher amounts of C, Cr, Si, W and Mo in SNCM8 or STD61. These elements retard the diffusion of boron. The growth rate of the boride layer increases linearly with increasing treatment temperature than and in a relatively lower treatment temperature 750°C it is not exactly definable because of showing a very thin boride layer. Boronizing of steel parts have been investigated by a variety of workers using a glow discharge with different mixtures of BCl_3 and H_2 [4-6]. The active atmosphere is usually diluted by argon or some other inert gas in order to enhance control of the BCl_3 concentration and to reduce the ignition voltage of the discharge. Fig.3 shows the variation of boride layers as a function of the amount of BCl_3 for the experimental conditions of treatment time of 4hr at 800°C.

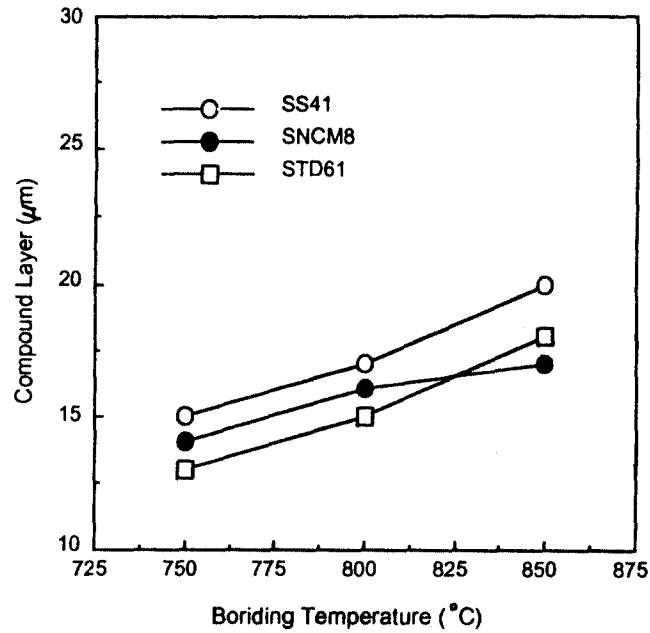


Fig.2 Variation of boride layer as a function of treating temperature, which were formed in the atmosphere of 0.25 vol% BCl_3 and 50% H_2 + 50% Ar for 4hrs

The boride layers depend strongly on the BCl_3 concentration. At low concentrations the growth rate of the boride layer is lower than that at high concentration of BCl_3 . If the BCl_3 concentration exceeds 0.5 vol% an exfoliation of the boride layer can occur even during the treatment itself.

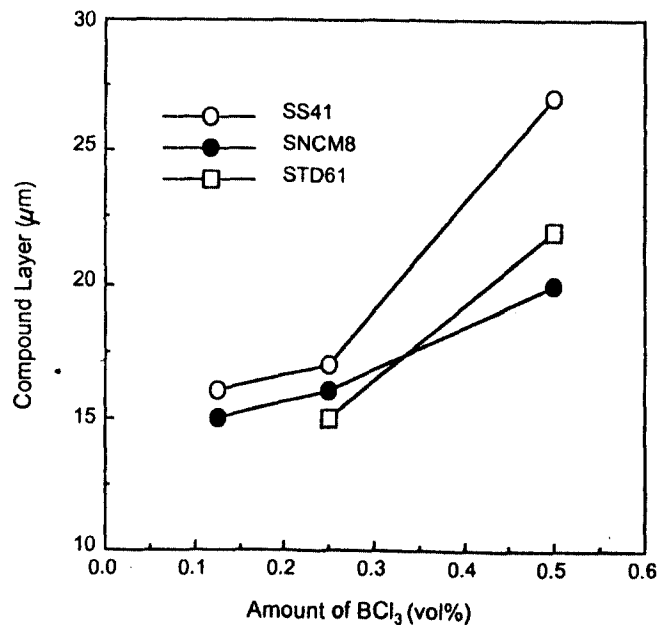


Fig.3 Variation of boride layer as a function of the amount of BCl_3 , which were for 4 hrs at 800°C

Kinetics of boride layer growth on SS41, SNCM8, and STD61 were studied at 800°C. The overall growth obeyed a simple $t^{1/2}$ relationship as shown in Fig.4. These results indicate that the growth kinetics is diffusion controlled. With gaseous atmospheres composed BCl₃ and H₂ plasma boronized layer with an equiaxis structure were achieved. This structure is made perfectly visible by means of scanning microscope. Fig.5 shows as an example the structure of such a layer obtained at SNCM8 steel. Fig.6 shows a diffractogram of the boride layers obtained in the plasma atmosphere of 0.25 vol% BCl₃ for treatment time of 4hrs at 800°C. This series of X-ray patterns shows that the Fe₂B phase appears primarily.

Several investigations of plasma boronizing processes have been previously reported that the boride layer composed of FeB and Fe₂B phases[7-8]. And it is very well known that Fe₂B phase hardens the surface more than the FeB phase. In our studies, we could obtain the all most of Fe₂B phase and know that the amount of atomic boron available may play an important role in determining which phase is formed. Therefore plasma boronizing allows the proportion of BCl₃ to another carrier gases to be changed, which may alter the formation of the two phases to favor one phase over another.

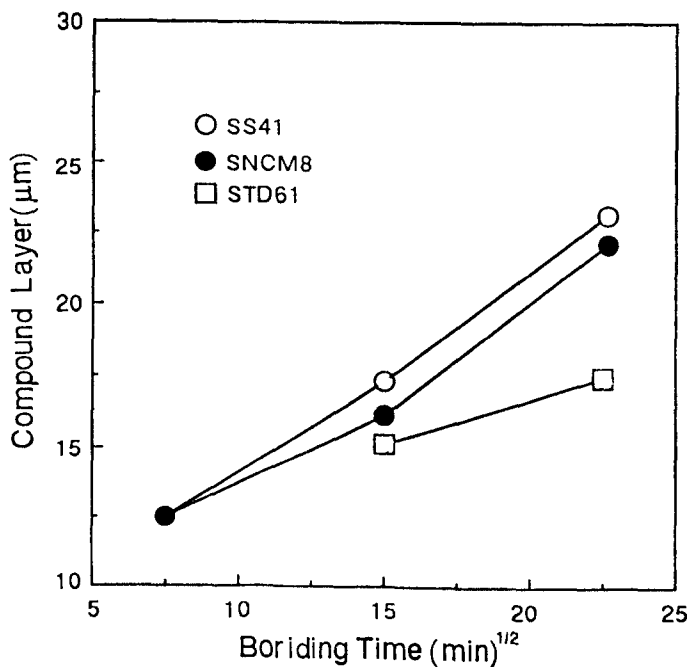


Fig.4 Variation of boride layer as a function of treating time, which were formed in the atmosphere of 0.25 vol% BCl₃ and 50% H₂ + 50% Ar at 800°C

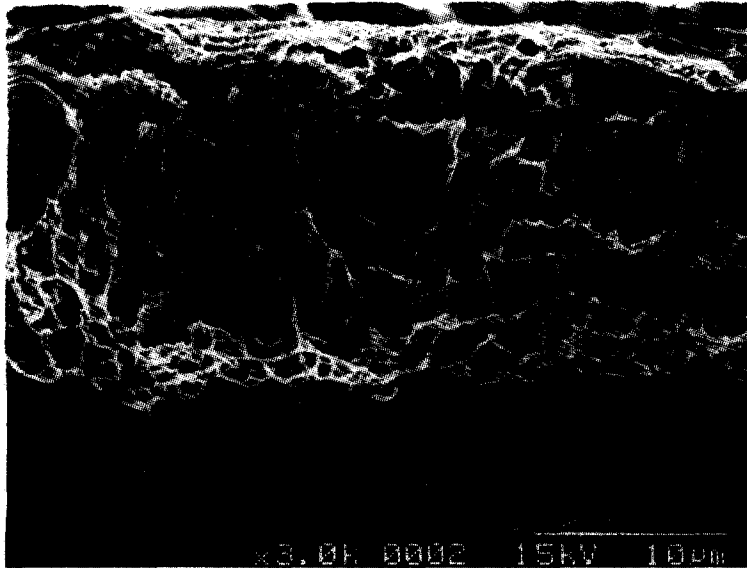


Fig.5 (a) Scanning electron micrographs of the fracture surface of the SNCM8 steel, which were boronized in the atmosphere of 0.5 vol% BCl_3 and 50% H_2 + 50%Ar for 4hrs at 800°C. (b) Enlargement of the region A of Fig.(a)

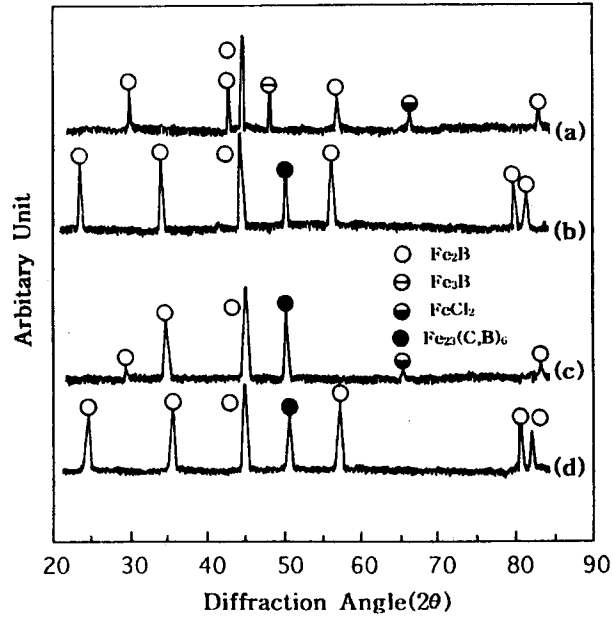


Fig.6 X-ray diffraction patterns of boronized layers with BCl_3 conc. (a) and (b) of SS41 steel were respectively formed from 0.125 and 0.25 vol% BCl_3 4hrs at 800°C . (c) and (d) of STD 61 steel were respectively formed from 0.125 and 0.25 vol% BCl_3 4 hrs at 800°C

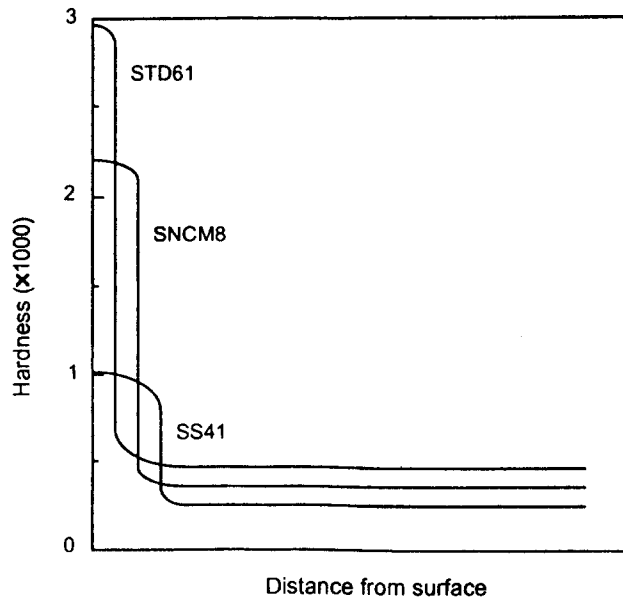


Fig.7 Hardness distribution across the boride layer of SS41, SNCM8 and STD61 which were formed in the atmosphere 0.25 vol% BCl_3 and 50% H_2 + 50%Ar for 4hrs at 800°C

To evaluate the effect of alloying elements on the extent boron dissolution, microhardness traverses were carried out on STD61, SNCM8 and SS41 which has been borided in the atmosphere 0.25 vol% BCl₃ and 50%H₂ + 50%Ar for 4hrs at 800°C. Fig.7 shows that maximum surface hardness of STD61 steel is about 2700kg/mm². However, in the case of SS41 steel, this value is about 1000kg/mm². The results in the present work illustrates that surface hardening mechanisms are closely related with the formation of Fe₂B phase and borides of another alloying elements, and the rate controlling mechanism in the growth of boride layer is diffusion of boron through the production layers.

4. Conclusions

1. SS41, SNCM8 and STD61 steels were successfully plasma boronized and the process parameters established for small components.
2. Various boride layer, Fe₂B, Fe₃B, Fe₂₃(C,B)₆ were identified by X-ray diffraction.
3. Plasma boronizing offers a hard case of as high as 2700kg/mm² as compared with 500kg/mm² of the core for STD61 steel.
4. Micro hardness measurement and optical microscopy indicate that the growth rate of boride layer is controlled essentially by the diffusion of boron through the boride layers.

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