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The Formation of Hexagonal Boron Nitride on the Surface of Stainless Steel by Chemical Vapour Deposition

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Abstract: Boron was deposited on stainless steel by Chemical Vapor Deposition (CVD) from a gaseous mixture of B_2H_6 (diborane) with a mixture of argon and hydrogen. The SEM and EDX studies showed that an amorphous uniform layer of boron was obtained Thickness measurements were carried out using a Dektak profilometer. A minimum thickness of 2200 Å was obtained.The boron enriched steel was annealed at 1050°C and then quenched in water in order to avoid any precipitation (especially that of BN). Isothermal anneals were then carried out and Auger Electron Spectroscopy (AES) was used to study surface precipitation. The studies on the material isothermally annealed at 750°C indicated that precipitation of hexagonal Boron Nitride (hBN) took place on the surface of the stainless steel. This precipitation is not observed if the annealing temperature is greater or equal to 800°C. From the obtained data, a three-stage mechanism of BN precipitation on the surface of stainless steel was put forward. A precursion stage during which nitrogen and chromium atoms co-segregate to the steel surface. Then, superficial nitrogen atoms react with those of boron which migrate by diffusion, to form hBN. Finally, the hBN compound thus formed grows layer by layer starting from the interface.

Key words: Boron, nitride, stainless, steel, CVD, AES, SEM, EDX

INTRODUCTION

Boron and nitrogen form a compound, BN, which exists in different forms: amorphous or crystalline (hexagonal or cubic). In this research we are only interested in the hexagonal form. This latter is sometimes called «:white graphite:» because of its strong analogy with graphite (number of electrons, spatial group and sheet structure). Hence, the two have nearly analogous properties.

Hexagonal Boron Nitride (hBN) presents a planar lamellar structure of 6 alternating B and N atoms. All atoms are exactly superposed to form rows perpendicular to the sheets on which B and N alternate (Fig. 1). The structure of hexagonal boron nitride proceeds, not from the deformation of the cubic structure (of diamond type), but curiously from the deformation of a hypothetical boron nitride having a wurtzite type structure (Meersshe and Fenau, 1984). In graphite, which proceeds from a deformation of the diamond structure, the sheets planes succeed one another with a certain lag (Fig. 1). This difference is due to the probable existence of a small attraction between B and N atoms, usually of different electronegativities.

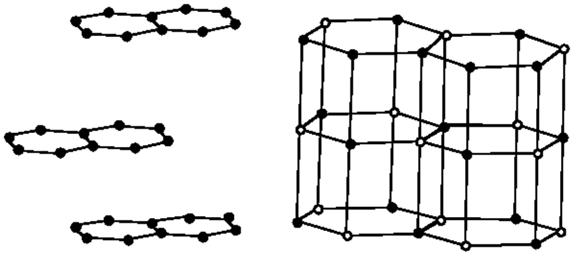
Fig. 1: Graphite (left) and hexagonal boron nitride (right)

Hexagonal Boron Nitride (hBN) was prepared for the first time by Balmain (1844). It is produced either in powder form (Lipp *et al.*, 1989) or in the form of thin layers by chemical vapor deposition or ion implantation (Bazi and Sknystautas, 1993). The technique used in this work is Chemical Vapour Deposition (CVD).

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MATERIALS AND METHODS

The steels used are industrial alloys obtained from Ugine S.A. (France) and Aubert et Duval (A and D, France). The chemical compositions are given in Table 1.
Both steels are rich in nitrogen. The A and D steel is a 316 type and the Ugine steel is a 304 type. Both steels have a f.c.c crystal structure. The Ugine steel can undergo a f.c.c. to c.c. transformation under the influence of cold work, whereas the A and D steel is very stable.

Experimental procedure: The method consists of depositing boron from a B_2H_6 (diborane) compound by CVD, followed by an anneal. Boron dissolves and diffuses into the steel. The result is a thin layer which should keep its adherence on the substrate for further manipulations (Fig. 2). The substrate is kept at high temperatures (800-1000°C).

Experimental details: The CVD reactor is of low pressure dynamic type (Fig. 3). It is made of three main parts:

Table 1: Chemical composition (in mass%) of the studied stainless steels

Element	A and D	Ugine
C	0.028	0.021
Si	0.59	0.485
S	<0.02	0.005
P	<0.025	0.023
Mn	1.73	1.333
Ni	12.78	6.6
Cr	17.61	17.5
Mo	2.72	0.179
Cu		0.077
Co	<0.1	0.149
Ti		0.002
Nb		0.004
V		0.073
Al		0.001
B	<0.002	0.0005
N	0.164	0.142

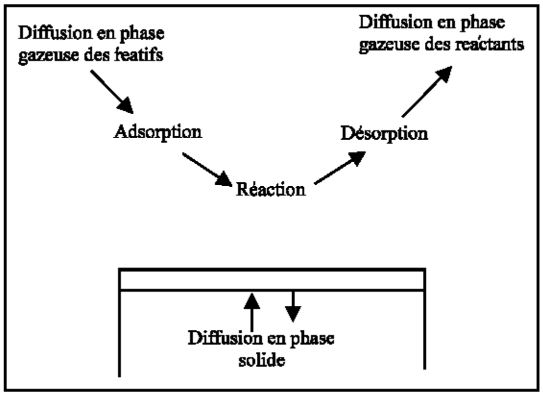

Fig. 2: Schematic representation of chemical deposition from a gaseous phase

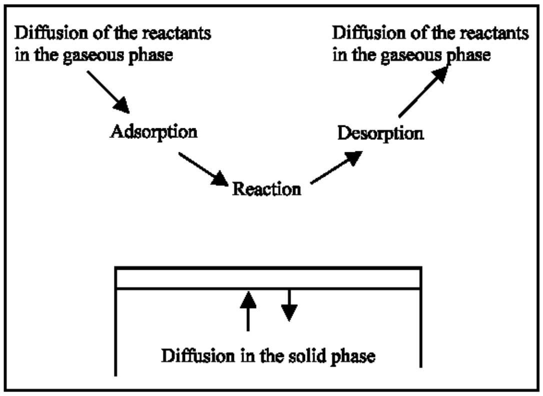

Fig. 3: Schematic representation of the used CVD reactor

- A vacuum area where the reaction takes place and the temperature is set at the desired value.
- A regulator which controls the pressure inside the vacuum area
- Another regulator which regulates the different gases entering the vacuum area.

The temperature should be high enough to allow the decomposition of the diborane to boron according to the following reaction:

$$B_2H_6\ (gas) \xrightarrow{\qquad} 2B\ (solid) + 3H_2\ (gas)$$

The two gaseous components that were used are diborane and a mixture of argon and hydrogen. The Ar/H_2 mixture (95%Ar, 5%H_2) enables the transportation of the reactive species, while maintaining a reducing atmosphere in order to avoid any oxidation and explosion problems (diborane reacts violently with oxygen). The variation of these two partial pressures leads to the modification of the deposit.

The regulation of the total pressure is provided by a pumping system (a two stage pallet pump, 15 $m^3\ h^{-1}$ flow rate, 2 mbar aspiration limit) coupled with a butterfly vane. The deposition duration is optimized during a series of trials in order to obtain a thin layer of desired thickness. An important experimental parameter is the limit vacuum. It is the minimum residual pressure after closing the chamber and in the absence of any gas flow. It conditions the m aximum amount of impurities present in the chamberduring deposition (a limit vacuum of 1.3 Pa for a total working pressure of 1.3×10^2 Pa corresponding to a maximum amount of impurities of 1%). The optimum working parameters are gathered in Table 2.

Table 2: Boron deposition conditions in the CVD reactor

Total pressure	2.66×10^2 Pa
Ar/H_2 flow rate	200 sccm
B_2H_6 flow rate	20-30 sccm
Temperature of the reactor	450°C
Depositing duration*	5-30 min.

RESULTS AND DISCUSSION

The EDX and SEM studies show that a uniform layer of boron from both the structure and the composition viewpoints is obtained (Fig. 4). The crystallographic analysis of the deposit shows that it is amorphous.

It is primordial to know the thickness of the deposited layers, since it determines the mass% of boron added to the steel. Thickness measurements were carried out on a reference boron layer deposited on glass. A profilometer (Dektak ST) having a diamond tip and a 10 Å resolution was used. A 2200 Å minimum thickness was obtained (Fig. 5 and 6).

The specific mass of the deposited boron layer is very near to the theoretical value (2.34 g cm^3). The calculation was done by weighing the deposit mass on a determined surface and by measuring the area of that surface. Table 3 contains some measured values and the resulting boron concentrations.

The adherence of the boron layers greatly depends on the surface quality and on the atmosphere in which the deposit is kept. The surface of the as received cold rolled Ugine steel (Ra = 570 Å) gave a good adherence, whereas the A and B steel required polishing so as to obtain a minimum roughness (Ra = 1800 Å). On the opposite, glass ave a good adherence with a roughness of only Ra = 29 Å. The coated specimens were kept in a dry medium. The qualitative and quantitative control of the CVD deposited boron layer allows the control of the boron quantity supplied to the steel.

Study of the surface chemistry of the steel: The steels enriched in boron by CVD, were annealed at 1050°C and then quenched in order to avoid any precipitation (particularly of boron nitride). The study is carried out in the following subsequent stages:

- A study of surface precipitation of BN during isothermal anneals,
- A particular interest is then given to the influence of sulfur on precipitation,
- The study is finally concluded by an attempt to understand the mechanism of BN precipitation.

Study of the precipitation: The study is carried out by Auger Electron Spectrometry (AES). The experimental procedure is detailed elsewhere. The specimen is

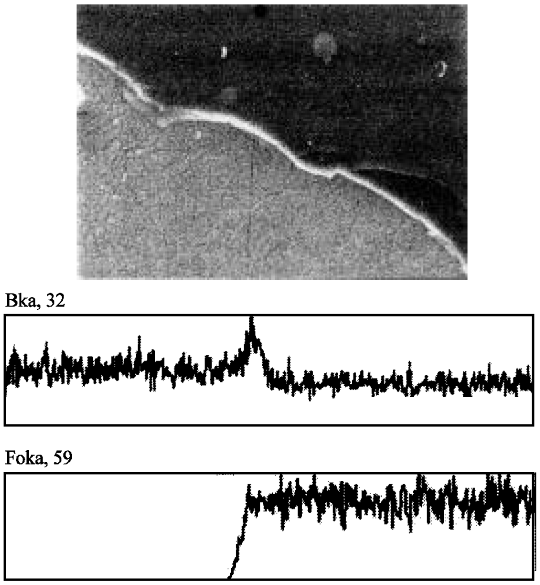

Fig. 4: EDX line on 77.44 µm on boron layer and substrate

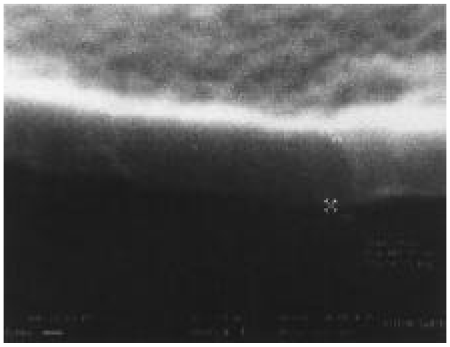

Fig. 5: Thickness of a boron layer (400 nm). Secondary electrons image

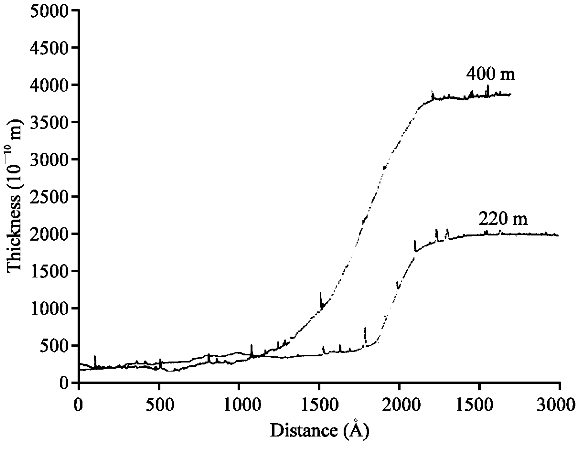

Fig. 6: Thickness of the boron layer measured with a profilometer

annealed, following cleaning of the surface by ionic bombardment at ambient temperature. The results presented are those obtained at 750°C. At this temperature the observations are identical to those made on the as received steel; namely:

- Nitrogen-chromium co-segregation, in a transient manner, during heating,
- Segregation of phosphorous,
- Phosphorous-sulfur competition,
- Segregation of sulfur.

However, a simultaneous apparition of boron and nitrogen on the surface of the stainless steel is observed in the following conditions (Fig. 7).

At 750°C, as in the as received steel, nitrogen co-segregates with chromium during the ascent in temperature. The nitrogen peak is symmetrical (spectra 2 and 3 of Fig. 8). After 8 min. of isothermal anneal, a diminution of the chromium and a modification of the form of the nitrogen peak (it becomes asymmetric) are observed on spectrum 4. This change is accompanied by the apparition of the boron peak at 172 eV (spectra 4-6). This latter is greatly displaced (Fig. 7) with respect to the spectrum of pure boron (180 eV). During the isothermal anneal, the superficial concentrations of boron and nitrogen increase as shown by spectra 5 and 6.

The asymmetrical nitrogen peak associated to the chemical displacement of the boron peak by 8 eV is characteristic of the presence of hBN (Mostefa, 1994). This is due to the strong boron-nitrogen interaction in the hexagonal structure (Stulen and Bastasz, 1979). This form of peak is found in the Auger spectra of graphite (Shelton *et al*., 1974).

As a summary, it can be said that superficial hBN precipitation is observed at 750°C. This precipitation is not observed if the annealing temperature is greater or equal to 800°C. Moreover, if the BN layer is already present on the surface of the steel at this temperature (800°C), it re-dissolves in the volume. Boron does not seem to alter the behavior of other segregating elements; particularly sulfur. Segregation kinetics of sulfur remain identical to those observed on the as received steel. This is in agreement with the observations of Ladna (Ladna and Birnbaum, 1988) on sulfur segregation to the surface and to the grain boundaries of nickel as a function of the concentration of boron. In the following, the influence of sulfur on the precipitation of BN will be discussed.

Influence of sulfur: The AES study conducted on the steel at 750°C shows that the surface is covered with BN, which is sometimes associated with sulfur. In fact, two types of surface chemistry are observed:

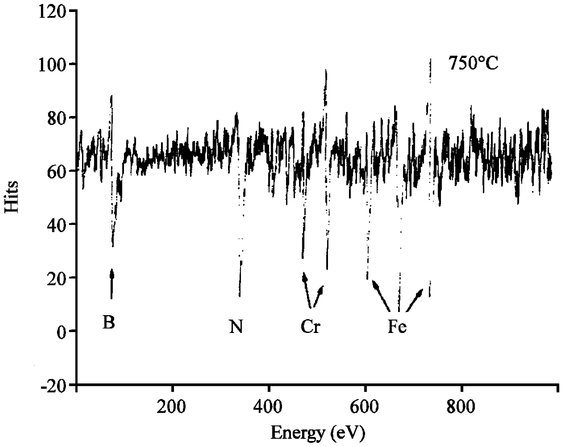

Fig. 7: Auger spectrum characterizing the presence of hBN on the steel surface at 750°C

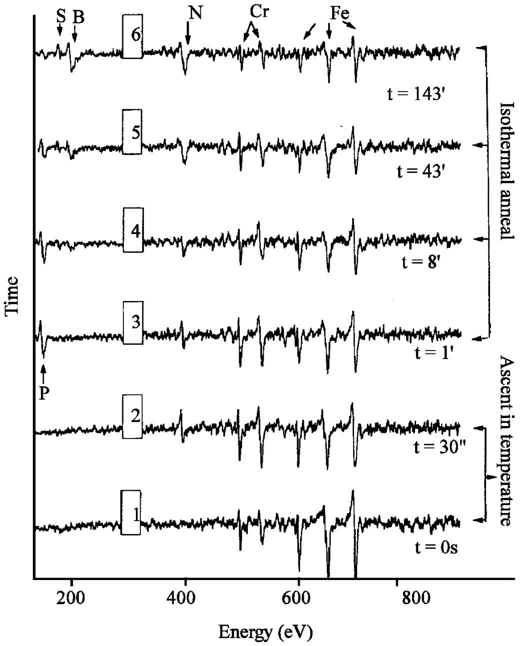

Fig. 8: Series of Auger Spectra during the ascent to and maintaining at 750°C

- That in which the sulfur peak is observed (spectrum b of Fig. 9) as well as the peaks of the substrate, indicating that the hBN layer is thin.
- That in which the BN layer is so thick (spectrum a of Fig. 9) that the substrate peaks are totally absent.

If an isothermal anneal is carried out at 800°C starting from the initial state, sulfur segregates to the surface. If the temperature is then lowered to 750°C, BN precipitation is observed (spectrum b of Fig. 10). In this case, however, the coverage with BN is not uniform, even after 25 h of isothermal anneal: the zones where sulfur has segregated during annealing at 800°C are not covered with BN as shown by spectrum a of Fig. 10.

This indicates that there is a competition between BN and sulfur that can be explained by the kinetics. If sulfur is already present on the surface (Fig. 10), it will prevent BN precipitation by a poisoning type mechanism of the necessary nucleation sites. If on the other hand BN appears first on the surface, it will occupy all the sites but will not prevent sulfur segregation (Fig. 12 a and b). In this last case, sulfur does not seem to segregate in the volume of the hBN layer, since it would then be visible on all AES spectra, whatever the thickness of the BN layer, which is not the case. It therefore segregates under the BN layer, at the steel-BN interface so that it is not detected if the layer thickness is important. It is only detected in the case where the substrate peaks are also observed, which indicates that the BN layer is very thin (~10 Å). In his work on the role of BN on high temperature ductility loss of FeNi 36, Ben Mostefa (1994) argues that BN, because of its lamellar structure, may be an adequate receiving structure for sulfur, by an intercalation mechanism. By means of ionic microscopy experiments, he clearly shows the S-BN association. Long and Grabke (1992) observe BN precipitation on the surface of FeNi 37. During surface oxidation experiments, they show that there is no surface oxidation if BN and sulfur are associated on the surface, whereas if they are separated, only the areas covered with sulfur undergo oxidation. In both cases, BN protects the surface from oxidation. They also carried out complementary ionic abrasion experiments on the BN covered alloy. Figure 11 shows that the intensities of the boron and nitrogen peaks diminish right from the beginning of the surface abrasion, whereas that of sulfur remains

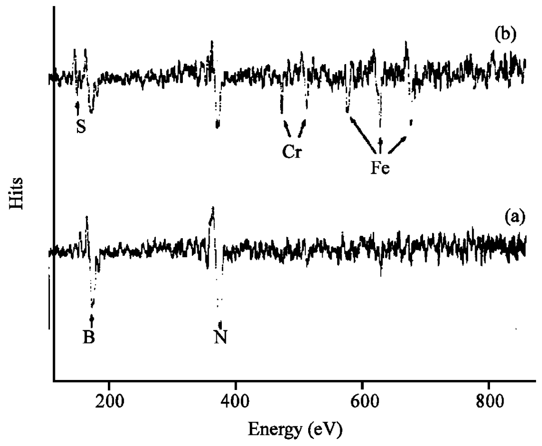

Fig. 9: Auger spectra from the stainless steel at 750°C

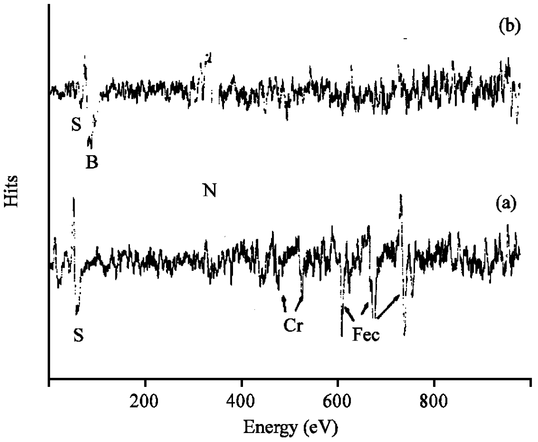

Fig. 10: Auger spectra from the steel surface after annealing at 800°C followed by a precipitation anneal at 750°C

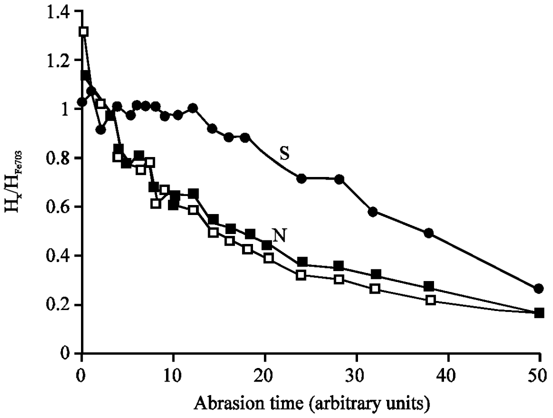

Fig. 11: Ionic abrasion profile showing that sulfur segregates under the hBN layer

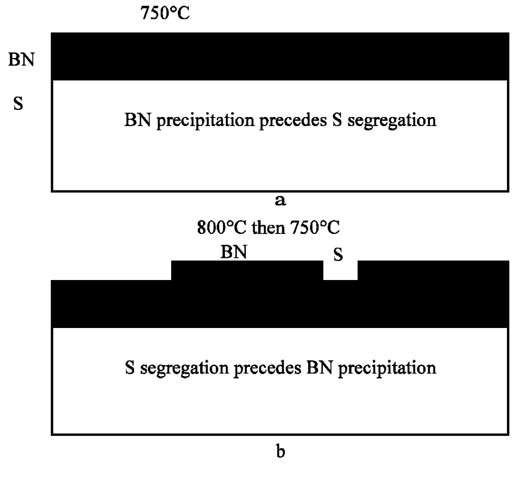

Fig. 12: Surface of the stainless steel

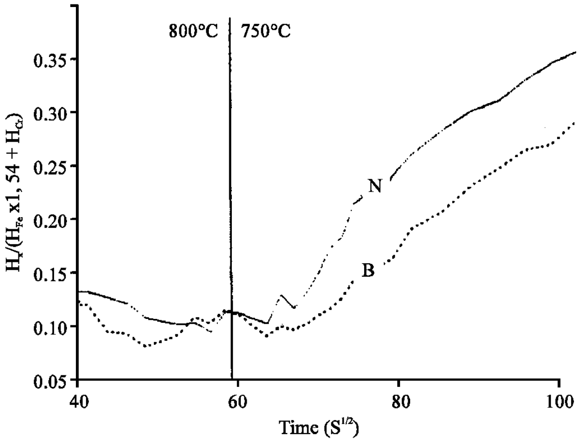

Fig. 13: Precipitation kinetics of N and B

constant despite the fact that sulfur is much more sensitive to abrasion than boron and nitrogen. It is only after a certain time that the sulfur profile too diminishes under the descaling effect. This indicates that the ion beam starts first by descaling the BN layer. They conclude that sulfur is situated under the hBN layer.

Sulfur segregates between the stainless steel and the BN layer, i.e., at the metal-ceramic interface. If BN precipitation precedes sulfur segregation, a uniform layer is obtained, otherwise sulfur occupies the BN nucleation sites and prevents precipitation as shown on Fig. 12.

Mechanism of BN surface precipitation: From data similar to those obtained in this research, Fujita (1989, 1992) puts forward a 3-stage BN precipitation mechanism on the surface of stainless steel:

- A precursion stage during which nitrogen atoms co-segregate, together with chromium, to the steel surface.
- Superficial nitrogen atoms react with those of boron which migrate by diffusion, to form hBN.
- The hBN compound grows layer by layer starting from the interface.

These different stages are well illustrated by the spectra of Fig. 8. This mechanism has only been observed on the surface of stainless steels (Stulen and Bastasz, 1979; Yashihara *et al*., 1985). On chrome-less alloys, such as FeNi (Ben Mostafa, 1994; Long and Grabke, 1992) or FeSi (Humbert *et al*., 1988) there is no trace of nitrogen segregation prior to BN precipitation. In order to verify this mechanism, an ionic bombardment was carried out at ambient temperature, followed by a first anneal at 800°C and a second one at 750°C, without returning to ambient temperature (Fig. 13). It is worth reminding that during the ascent to 800°C, nitrogen-chromium co-segregation followed by phosphorous segregation and then sulfur segregation were observed, but no hBN precipitation. At 800°C, the specimens are maintained until complete disappearance of the nitrogen resulting from co-segregation with chromium. The temperature is then lowered to 750°C. In these conditions boron and nitrogen appear together on the surface of the steel as shown in Fig. 13 whereas returning directly from 800-750°C, without passing by ambient temperature, made it possible to see nitrogen-chromium co-segregation. This experiment proves that no nitrogen segregation prior to the appearance of boron is necessary for BN precipitation and that the mechanism suggested by Fujita is only the result of a quicker chromium segregation, due to its high concentration, during the transient heating period. It also proves that contrary to observations on Invar (Ben Mostafa, 1994) activation of the surface is not necessary for BN precipitation on the surface of stainless steel, since the 1 h anneal at 800°C has eliminated the crystal defects created by the bombardment. Ion bombardment, a condition prior to precipitation as observed by Ben Mostefa (1994), is not therefore a necessary condition in stainless steels. If Ben Mostefa did not obtain superficial precipitation without activation of the surface prior to the anneal, it was probably because boron and nitrogen supersaturation in his alloy was not sufficient for BN precipitation on the surface without a prior reduction of the energy necessary to the nucleation of the precipitates by activation of the surface. In our case, a greater supersaturation in boron and nitrogen allowed superficial precipitation without prior activation during isothermal anneals, carried out in-situ inside the AES. It is worth mentioning that this type of experimentation is not reproducible if the heat treatments were to be carried out in silica capsules; in this case a BN layer is observed under SEM only if the surface was initially activated. Activation has therefore no effect on nucleation since the precipitation of a monatomic layer is observed under AES, but has an effect on the growth kinetics necessary to the obtainment of a thick layer (unless it is an effect due to sulfur).

CONCLUSION

An enrichment in boron of the stainless steel lead to the obtainment of a surface layer of BN, which precipitated on the entire surface of the steel during an isothermal anneal at atemperature between 750 and 800°C. Precipitation occurs by simultaneous diffusion of boron and nitrogen, according to a classical two step mechanism (nucleation and growth) and nitrogen segregation is not a necessary stage as reported in the literature. Moreover, BN precipitation on the surface of stainless steel does not require activation of the surface prior to annealing. Nevertheless, activation plays a role on the growth of the layer.

Sulfur seems to have a major role in that while it does not prevent precipitation, it segregates to the metal-ceramic interface, thus likely affecting the cohesion of the layer. Measurements of the adherence of the BN layer could be undertaken in order to evaluate the role of the segregated sulfur on the mechanical properties of the interface.

The results obtained in this work do, in no way, lead to think that nitrogen-chromium co-segregation and phosphorous segregation disturb surface precipitation of BN.

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