

## Surface modification and induced ultra high surface hardness by nitrogen ion implantation of low alloy steel

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A surface hardenable low alloy carbon steel was implanted with medium energy (20 – 50KeV)  $N_2^+$  ions to produce a modified hardened surface. The implantation conditions were varied and are given in several doses. The surface hardness of treated and untreated steels were measured using depth sensing ultra micro indentation system (UMIS). It is shown that the hardness of nitrogen ion implanted steels varied from 20 to 50GPa depending on the implantation conditions and the doses of implantation. The structure of the modified surfaces was examined by X-ray photoelectron spectroscopy (XPS). It was found that the high hardness on the implanted surfaces was as a result of formation of non-equilibrium nitrides. High-resolution XPS studies indicated that the nitride formers were essentially C and Si from the alloy steel. The result suggests that the ion implantation provided the conditions for a preferential formation of C and Si nitrides. The combination of evidences from nano-indentation and XPS, provided a strong evidence for the existence of  $sp^3$  type of bonding in a suspected  $(C,Si)_xN_y$  stoichiometry. The formation of ultra hard surface from relatively cheap low alloy steel has significant implication for wear resistance implanted low alloy steels.

**Key words:** Ion implantation, low alloy steel, surface modification, nitrides, ultra high hardness, Si doped carbon nitride

### 1. INTRODUCTION

Surface reaction techniques at high temperatures like carburising and nitriding are well established for surface hardening of steels in applications where high wear resistance is a functional requirement. The combinations of high modulus/ high hardness developed in such modified surface are fundamental to the development of wear resistance. These thermo-chemical treatments would normally lead to the developments metastable structures of carbides/nitrides and/or create the thermo-kinetic conditions for formation of martensites. The depth of hardened layer by conventional surface hardening can be of the order of mm, but the maximum harness attainable is generally less than 15GPa. Ion implantation of nitrogenous species has been used to produce harder surfaces. But the mechanism for hardening is still a subject of considerable debate. There is therefore a lot yet to be understood about the chemical compounds formed by ion beam modification, and the effects of base composition and implantation conditions on the chemical and mechanical properties of ion modified layer.

Here we present new evidence that ion beam modification could lead to a surface composition that forms a layer where ferrous species plays little role and where the presence of Si in substrate steel appear to promote the formation of a doped carbon nitride.

### 2. EXPERIMENTAL PROCEDURE

$N_2^+$  ion implantation was conducted on a 50keV ion implanter that consists of a Freeman ion source, a high voltage accelerator, a mass selection magnet, an electronic sweeper and an ultra high vacuum chamber. Surface analysis was performed in a combined AES/XPS PHI spectrometer using

non monochromatic Mg  $K\alpha$  radiation (1253.6eV) including Cylindrical mirror analyser (CMA). General surveys were done at pass energy of 50eV and higher resolution elemental surveys were done at pass energy of 25eV. The hardness of the surface was investigated by UMIS 2000, a micro-mechanical probe capable of obtaining force – depth data with force and depth resolutions of  $\mu N$  and nm respectively.

### 3. RESULTS AND DISCUSSION

The hardness values recorded for the  $N_2^+$  implanted samples under various implantation conditions varied from 35 to 50GPa. The hardness and the implantation conditions are given in Table 1. The values are higher than for conventional surface hardening treatments and for previously reported values for ion implanted steels[1,2] which are typically less than 15GPa.

It is thought that the high hardness observed on the surface of the steel was due to the chemical modification of the surface by the ion implantation. We therefore, employed the technique of XPS to study the chemical configuration of the modified layer and we particularly chose sample 3 (see Table 1) which showed the highest hardness for the XPS characterisation.

Sample No	Ion Beam energy (KeV)	Ion dose (ions/cm <sup>2</sup> )	Hardness (GPa)
1	33	$1.95 \times 10^{17}$	35
2	35	$4.3 \times 10^{17}$	45
3	20	$5.8 \times 10^{17}$	50
4	30	$7.8 \times 10^{17}$	40

Table 1: Implantation conditions and hardness

The general survey of the XPS indicated that the Fe lines are very weak for the implanted sample, even after 1 minute Ar<sup>+</sup> etching. Additionally, the implanted sample showed a relatively strong N and Si peaks. While the presence of N line can obviously be attributed to the effect of N<sub>2</sub><sup>+</sup> ion implantation process, the strong Si and the weak Fe signals (compared with as-received sample), suggests a massive micro alloying of the surface and subsurface regions.

The weak Fe signal was particularly surprising, and we sought to confirm this by detailed study of the Fe 2p lines. This examination showed that the Fe 2p line did not become strong until after 4 minutes of etching and only became well defined (as expected in a fresh un-implanted sample) after prolonged etching. This evidence confirms that Fe has little contribution to the chemical structure in the surface.

The present evidence strongly suggest that the surface chemistry was essentially dominated by C, Si and N, in a chemically modified layer through the implantation process by preferential selective chemical reaction between the incident N<sub>2</sub><sup>+</sup> and C and Si atoms from the steel substrate.

The existence of a carbon nitride layer would generally be consistent with the high hardness found. Similar increased hardness (though a somewhat lower value of 35GPa) has been reported in N doped diamond like films[3]. We further examined the nature of the C and N bonds in the modified layer and compared with current understandings in carbon nitride films.

The XPS C1s and N1s are shown in Figures 1 and 2 respectively. The C 1s peaks at 285eV and a full width half maximum (FWHM) of 4eV suggest it is coming from more than one source, most probably two, as indicated by the attempted curve fitting. Nevertheless, a peak centre close to 285eV is consistent with sp<sup>3</sup> type of C- bonds expected in crystalline C<sub>3</sub>N<sub>4</sub>[4]

The N1s peak (Fig 2) in particular, is more suited for the characterisation of the modified layer. The N1s spectrum peaks at 398.5eV with FWHM of 2eV. The FWHM is narrow and close to values of 1.7 – 1.8 that has been allocated [4] to nitrogeous species. The weight of this evidence suggests that the N signal is emanating largely from single N specie, peak-fitted at 397.8eV, in contrast to very wide N spectrum that has been recorded in several other attempts [4–6] at the synthesis of carbon nitrides. The use of XPS to identify the position of sp<sup>3</sup> bonded N in C–N layers has produced too many varied results[18], nevertheless, our present results showing N1s dominant peak at 397.8 is consistent with sp<sup>3</sup> bonded N as reported in refs [6 – 8].

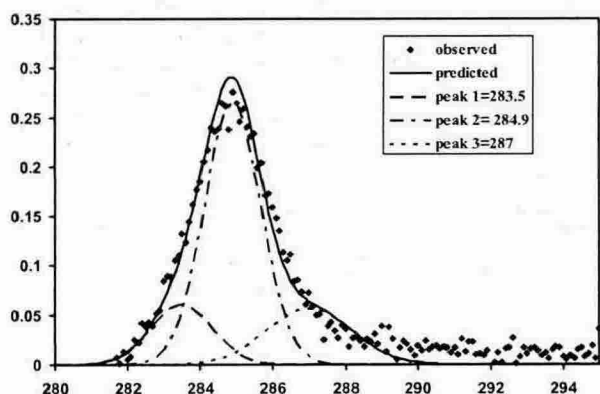


Fig. 1. C1s raw data, and fitted peaks

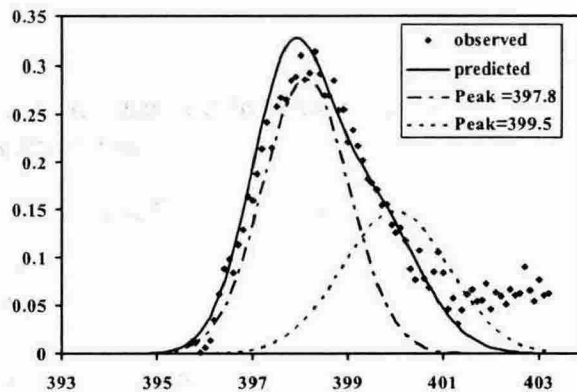


Fig. 2. N1s raw data, and fitted peaks

The role of Si in the formation of sp<sup>3</sup> bonds in C–N is considered to be significant and indeed thought to be part of the chemical configuration. Since Si<sub>3</sub>N<sub>4</sub> is analogous to C<sub>3</sub>N<sub>4</sub>, it is thought that the doping action of Si would promote the formation of sp<sup>3</sup> bonding expected in a compound nitride of the type (C,Si)<sub>3</sub>N<sub>4</sub>. It is well known for instance that Si<sub>3</sub>N<sub>4</sub> has been grown by ion implantation of N<sub>2</sub><sup>+</sup> into a Si substrate.

The combination of evidence from XPS and nanohardness therefore confirms that the ultra high hardness we observed from the ion implanted steel is as a result of the chemical modification of the surface of the steel by the implantation process. The origin of the hardness is due to the chemical structure of the carbon and nitrogen structure induced by the presence of small proportion of Si.

#### 4. CONCLUSIONS

The surface composition of low alloy heat treatable grade steel can be modified by N<sub>2</sub><sup>+</sup> ion implantation. The chemical reaction as a result of implantation led to the formation of nitrides of carbon and silicon. The hardness of modified surface was 35–50GPa depending on implantation conditions and was higher than that of N doped diamondlike films.

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