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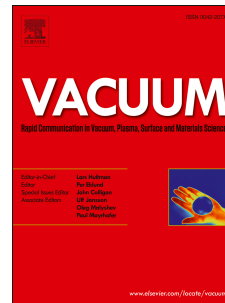
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# Accepted Manuscript

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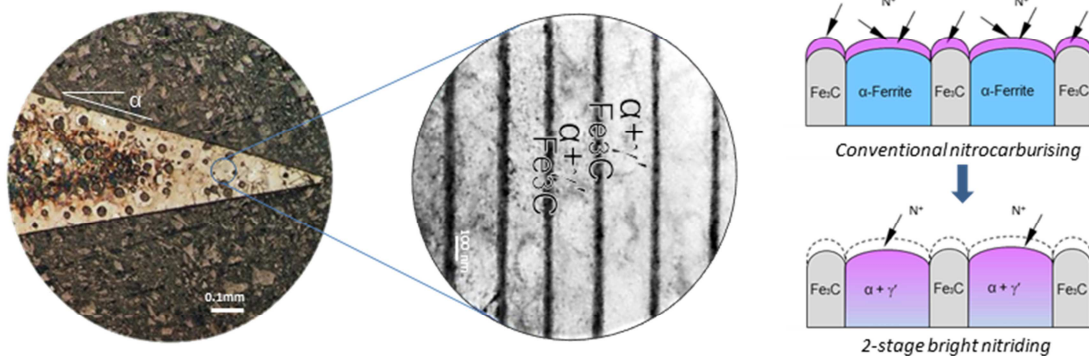
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## Abstract

To alleviate spallation and effectively hardened the spheroidal graphite cast iron, a diffusion-prevalent hardened case was produced on the spheroidal graphite iron surface by a new two-stage bright nitriding process. The unique feature of this process in treating the sharp edges with high strength and controllable layer thickness has been emphasised. An exceptionally deep diffusion layer of 300 $\mu$ m was produced during bright nitriding, and the formation and thickness of the compound layer were easily controlled in this continuous short nitriding process. The produced hardened case mainly composed by polyphase of  $\alpha$ /Fe<sub>4</sub>N, in comparison to the conventional Fe<sub>2</sub>N<sub>3</sub>/Fe<sub>4</sub>N of compound layer, are formed along the new pearlite laminae, which results in significantly improved surface hardness and corrosion resistance.



## Keywords

phase transformation; diffusion; nitriding; cast iron; hardness; surface hardening

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## 1. Introduction

Spheroidal graphite (SG) cast iron has been used as the tooling material for metal forming of high-strength light-weight alloys for the automotive industry. Surface modification with plasma nitrocarburising has been recognised as an effective method for improving the wear and fatigue resistance and of the SG cast iron surface [1-3]. However, because of the specific geometry of sharp angles on complex shaped dies and tools, they are difficult to be successfully treated using conventional nitrocarburised process. These thermochemical processes generally produce superior hardening effect by the formation of intermetallic  $\text{Fe}_{2-3}\text{N}$  and  $\text{Fe}_4\text{N}$  phases [2, 4]. For cast irons, the formations of  $\text{Fe}_{2-3}\text{N}$  and  $\text{Fe}_4\text{N}$  phases grow almost only in the lateral direction to form a closed compound layer which impedes the further diffusion of elements. Consequently, the formed compound layer is very thin [5]. In addition, the compound layer has a regional porous microstructure, resulting in a poor adhesion of the layer on the substrate in these inhomogeneous regions [6]. The latter can cause the chip and spallation of the brittle compound layers in the regions where shear stress concentrated, such as the sharp edges or the corners of complex shaped dies and component.

With the aim of increasing the strength and toughness of sharp edges of tools, researchers have tried avoiding this thin layer completely. Early work by Floe, Bell and Lightfoot reduced the formation of compound layer on steels by altering the gas composition [7]. Bright nitriding using a low level of nitrogen potential and a prolonged nitriding cycle has been used for hardening steels without the formation of compound layer. Recently, lowering the nitriding temperature [8], or using another hardening method of nitriding+boriding [4] are effective approaches to produce diffusion layers. The latter can produce better case depth than the other methods but requires non-continuous treatments, and extra handling of powder-pack. To this end, little evidence has shown the controlling of compound layer growth on cast irons which have no nitride-forming elements (e.g. Cr, Al). The objective of this study is to manage the thickness of both diffusion layer and compound layer for SG cast iron, by using a continuous and easy-to-control double-stage bright nitriding (DSBN) process. The produced duplex hardened case should have a controlled layer structure, and a balanced hardness and toughness on the surface layer that is suitable for the sharp wedges.

## 2. Material and methods

SG cast iron (automotive metric standard D6510/NAAMS with nominal composition (wt%, 3.2 C, 2.6 Si, 0.8 Mn, 0.4Mo, 0.10 Cr, balance Fe) was cast and stress relieved at 690 °C for 2 h, followed by machining, polishing to roughness  $R_a=0.1 \mu\text{m}$  prior to plasma treatments. The treatment conditions are summarised in Table 1. Bright nitriding was carried out in a pulsed plasma furnace with reduced nitrogen potential and prolonged treatment time compared to conventional nitrocarburising for SG cast iron [2], which is tested as a comparison in this study. Some samples were treated with DSBN processes: 1) bright nitriding, followed by 2) short nitriding, continuously in a pulsed plasma furnace. The treated specimens were cut with MetPrep SiC cut-off wheel and then Bakelite mounted and ground to a 1200 grit finish using an automatic Struers polishing wheel, followed by polishing with  $9 \mu\text{m}$  and  $1 \mu\text{m}$  diamond solution on a Struers DP-Dur cloth. Immediately after polishing, the specimens were etched in 3% Nital and the microstructure was examined by a field-emission scanning electron microscope (FE-SEM, JEOL 7000). Crystallography was identified via X-ray diffraction (XRD) equipped with a  $\text{Cu-K}\alpha$  radiational source, operated at 40 kV. The X'Pert High Score software with the PCPDFWIN database was used to identify the presence of crystalline phases in the coating. Quantitative composition and thickness of the hardened case were measured by the glow discharge optical emission spectrometry (GDOES). Vickers microhardness (Mitutoyo mVK-H1 micro) was used with a load of 0.025 kg to measure the surface hardness of the treated surfaces following the ASTM E92 standard.

Table 1 Conditions of surface treatments

Sample	Processing	Stage I					Stage II				
		$T, ^\circ\text{C}$	$t, \text{hours}$	Pressure, mbar	Gas	Current, A	$T, ^\circ\text{C}$	$t, \text{hours}$	Pressure, mbar	Gas	Current, A
BN	Bright nitriding	545	24	1	$\text{N}_2$ 5% $\text{H}_2$ 95%	42	-	-	-	-	-
NC	Nitrocarburising	-	-	-	-	-	575	24	1	$\text{N}_2$ 50% $\text{CH}_4$ 2% $\text{H}_2$ 48%	60
BN+N30	Bright nitriding plus nitriding	545	24	1	$\text{N}_2$ 5% $\text{H}_2$ 95%	42	525	0.5	1	$\text{N}_2$ 25% $\text{H}_2$ 75%	40
BN+N60	Bright nitriding plus nitriding	545	24	1	$\text{N}_2$ 5% $\text{H}_2$ 95%	42	525	1	1	$\text{N}_2$ 25% $\text{H}_2$ 75%	40

### 3. Results and Discussion

The metallography and layer structures of SG cast irons are shown in Fig. 1. Some features of the materials microstructure can be observed from the metallography. SEM cross-section micrograph in Fig. 1d shows that a deep diffusion layer of 300  $\mu\text{m}$  can be produced by the bright nitriding process, compared to the <150  $\mu\text{m}$  thickness of the hardened case on a typical nitrided cast iron [9]. This ultra-thick hardened case was formed during bright nitriding and uniformly covers the sharp edges as shown in Fig. 1d. As for the outmost layer, the thickness of the compound layer is determined by the nitrogen potential in the atmosphere. As shown in Fig. 1e and 1f, the BN sample is free from any compound layer on the top surface, which means that the hardened case is only composed of the diffusion layer. After the subsequential nitriding for 60 mins, the compound layer with the thickness of 12  $\mu\text{m}$  appears on top of the diffusion layer, so to create a dual-layer structure. The dual layer construction will benefit the toughness of the surface, which is critical for the toughness and performance of the sharp edges. Using the double-stage plasma process, the thickness of the compound layer is controllable without affecting the total thickness of the diffusion layer.

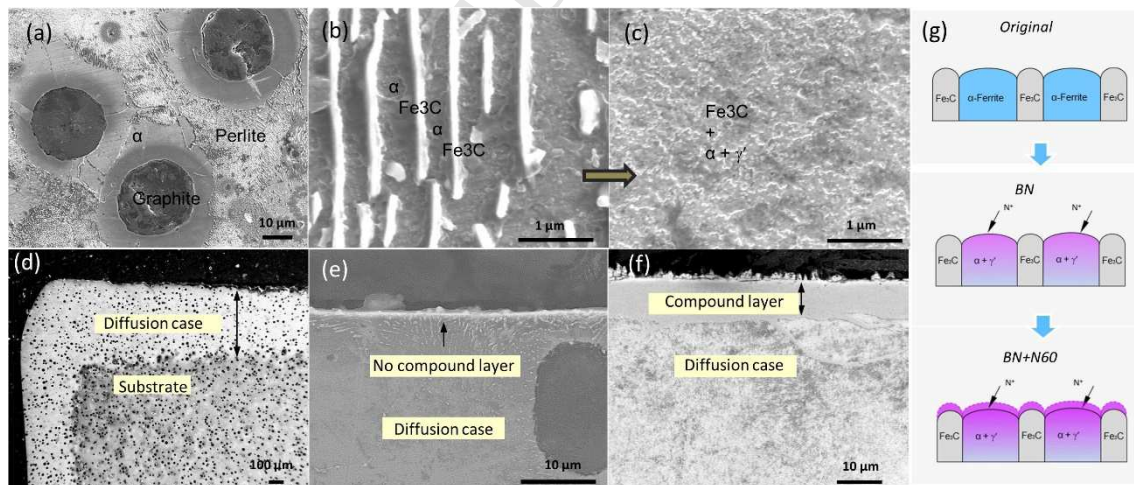


Fig.1. SEM images of (a) as-received SG cast iron, and (b) original pearlite, (c) BN treated pearlite, (d) hardened case around a BN treated edge, and (e) the enlarged view of hardened case on BN and (f) on BN+N60, and (g) illustration of the phase transformations during different treatments.

A comparison of the enlarged views of the perlite area shows that the treated material is clearly etch-resistant and strikingly less contrast after the bright nitriding. Fig. 1b and Fig. 1c reveal that the original lamellar structure of the cementite and ferrite in pearlite in SG cast iron has lost its contrast after treatment. The newly formed pearlite microstructure is dull but still shows very fine features and it is not as smooth as the white layer. Disappearing of the contrast between these two phases is probably because of the transformation of ferrite in the lamellar to the etchant-resistant iron nitrides. Since both iron nitrides and carbide (i.e. cementite) exhibit similar corrosion resistance, the morphology of etched new pearlite shows less contrast. This also means that after bright nitriding, the SG cast iron becomes more etchant resistant as an indication of the increased resistance to corrosion.

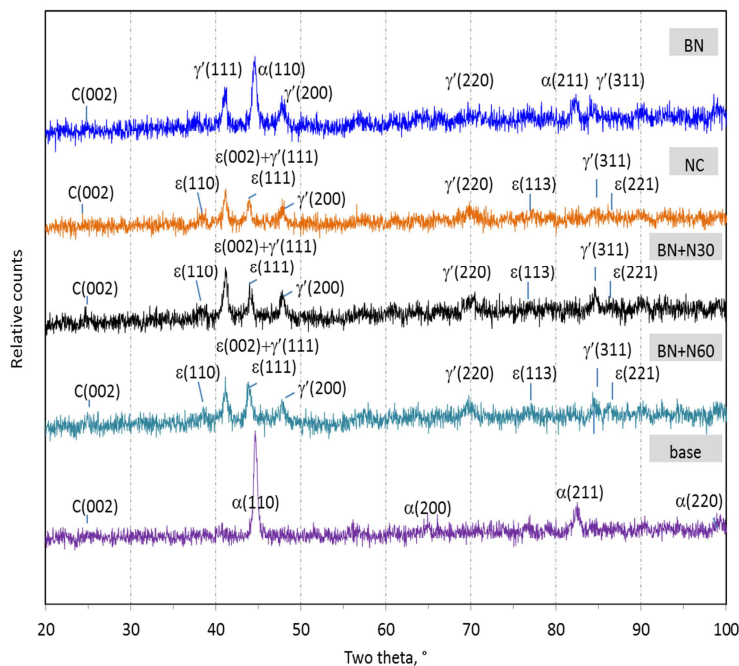


Fig.2. XRD spectrum of treated and untreated SG iron surfaces

The modifications in phase constitution after plasma treatments are shown in the XRD spectra in Fig. 2. The original SG cast iron is composed of mostly  $\alpha$ -Fe. After bright nitriding, the appearing of  $\gamma'$ -Fe<sub>4</sub>N at 41° and 48° on BN suggests the partial transferring of microstructure from  $\alpha$ -Fe to  $\gamma'$ -Fe<sub>4</sub>N. Since the compound layer is not present on the surface, the  $\gamma'$  is expected mainly existing between the new pearlite laminae. As for NC, BN+N30 and BN+N60, a polyphase of  $\gamma'$ -Fe<sub>4</sub>N and  $\epsilon$ -Fe<sub>2-3</sub>N matches the microstructure of duplex layer of the compound layer and the diffusion case, and the disappearing of the original main peak of  $\alpha$ -Fe at 44.7° suggests that the substrate completely transferred from  $\alpha$ -Fe to

the compound layer on the superficial surface. Much research reported that only a mono-phase of  $\gamma'$  was produced by conventional plasma nitriding for cast iron [10-12]. The forming of a polyphase of  $\gamma'+\varepsilon$  at 41.2° and 44.0° is probably due to the stabilising effect of the higher concentration of carbon on  $\varepsilon$  as has been reported [10].

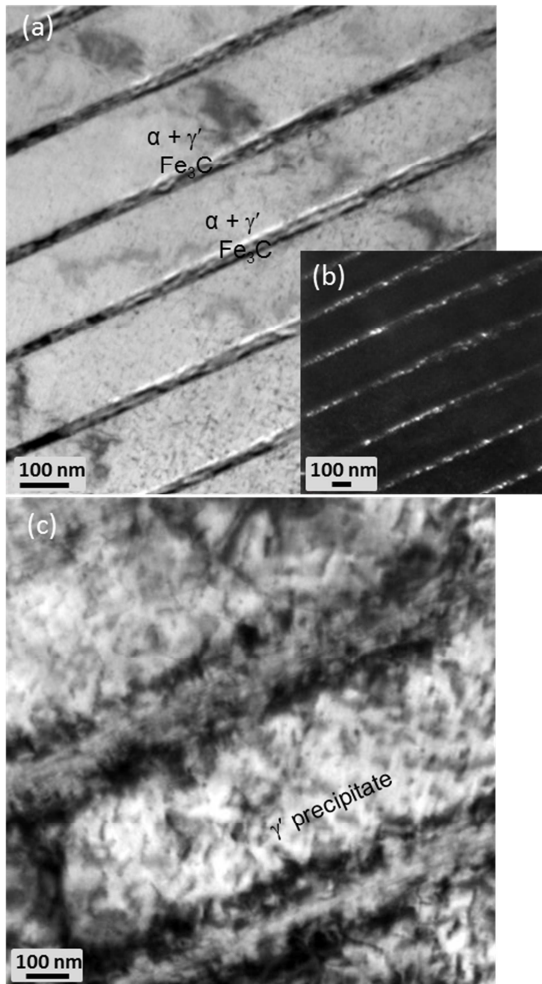


Fig.3. (A) bright field (BF) TEM images and (b) dark field (DF) images of the diffusion layer on the sample BN showing the new perlite laminae and (c) the high-magnification image of the  $\gamma'$  precipitates inside laminae.

Fig.3. shows the transmission electron microscopy images depicting the diffusion case of the bright nitrided only sample. There is no compound layer on the BN cast iron surface. The periodic layer arrangement in the bright image shows that the treated carbides always appear dark after double-tilting, due to the mass-thickness contrast on this homogeneous areas. In DF image, the treated carbides in different layers appear consistently bright-coloured which verified the consistent orientation of



carbides between each layer. The precipitates of  $\gamma'$  existing inside the layer of  $\alpha$  can be seen on the high magnification image and the size of precipitates is 5-10 nm. Similar to the carbides precipitates, the nitride precipitate of  $\text{Fe}_4\text{N}$  cannot be weakened by double-tilting, indicating the mass-thickness contrast of precipitate in relation to the  $\alpha$  matrix.

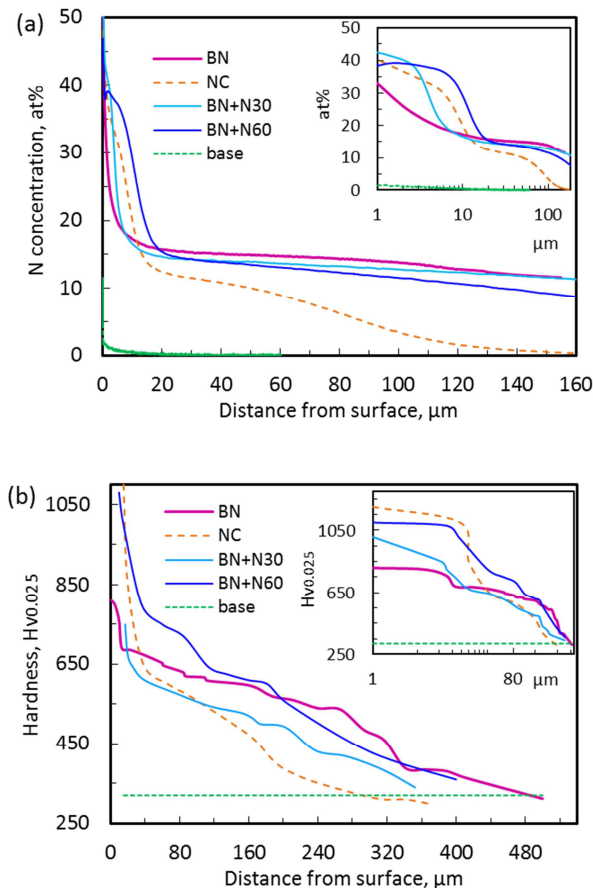


Fig. 4. (A) the elemental distribution of N, and (b) hardness profile of base and treated surfaces; (inserts) logarithmic scaled graphs showing the enlarged view of the outmost layer

The hardness of the DSBN treated surface and the corresponding element-depth profile is shown in Fig. 4. Since the strengthening of SG cast iron by nitrogen is proportional to the number of nitrides precipitates, the hardness and N mol% exhibited similar trends: after DSBN process, the surface hardness and elemental depth profile are improved significantly compared to that of the conventional NC. Although GDOES has good accuracies for N and can be applied to depth profiling up to about 100  $\mu\text{m}$ , the thickness of diffusion layer is out of range for BN+N30 and BN+N60. In addition, when a two-stage bright nitriding was used on BN+N30 and BN+N60, the plateau appears in the outmost layer of 10

$\mu\text{m}$ , matches the composition of a compound layer, as shown in the inserts. As a result, the hardness in this region reaches 1100Hv0.025. It is therefore believed that a dual-layer hardened case has been produced on the DSBN treated SG cast iron, which matches the cross-section microstructure shown in Fig. 1. The reason for the formation of a compound layer on the BN+N30 and BN+N60 is that when nitrogen species reaches the sample surface more than diffusing into the matrix, a compound layer formed only on the outmost layer. Since there is barely any nitrogen-absorbent element (e.g. Cr) in the cast iron substrate, it is difficult for the nitrogen to diffuse further; consequently, for the conventional nitrocarburising, the hardened case on cast iron has no adequate thickness [1, 13]. In contrast, during a DSBN process, the formation and thickness of compound layer is easily controlled by firstly inhibiting the formation of  $\text{Fe}_{2-3}\text{N}$  and  $\text{Fe}_4\text{N}$  at the very beginning of process, so that the diffusion of nitrogen can be continued; secondly, delaying the forming of compound layer to the end of the process, so that it does not interfere with the production of the diffusion layer in the first step and this is critical to the retention of the toughness and the wear resistance of the nitrified layer on the sharp edges of the treated cast iron. On the other hand, the graphite in the cast iron makes the surface of cast iron porous. During plasma nitriding, the active N atoms and precursors generated in plasma above the cathode are the primary species for plasma nitriding. They cannot penetrate small cavities and micro-pores on the surface of cast iron. Therefore, the range of mobility is very limited. Large-sized nodular graphite might be beneficial to the diffusion depth of nitrogen to overcome the primary drawback of lack of alloying element in cast iron, however, more studies need to be carried out. This study shows that DSBN process has significant advantages over conventional nitrocarburising since a combination of the toughness of diffusion layer and the hardness of compound layer can be obtained.

#### 4. Conclusions

This study described the development of a bright nitriding process in order to produce a thick hardened case for the sharp edges of spheroidal graphite cast iron. It was achieved by inhibiting the formation of  $\text{Fe}_{2-3}\text{N}$  and  $\text{Fe}_4\text{N}$  at the very beginning of the process by using a reduced amount of nitrogen, and then, finish with a shot stage of nitriding. The results of the presented research indicated that the formation of the diffusion layer and the total thickness of the dual layer is determined by the nitrogen potential in the atmosphere and a reduced potential during the first step is essential to create a thick diffusion layer.

This continues two-stage bright nitriding process is proven effective in forming a dual layer with an adequate thickness of the hardened substrate on cast iron which is critical to the retention of the sharp edges of cast iron component. The beneficial improvement on layer thickness, surface hardness and corrosion resistance was found derived from the delaying formation of compound layer to the end of the process and encourage the production of Fe<sub>4</sub>N at the first stage of treatment.

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**Highlights**

- A method of creating a duplex hardened case with controllable compound layer for SG cast iron
- The mechanism of suppressing formation during bright nitriding process has been explained
- The dual-layer microstructure with transformed perlite phase is significantly corrosion resistant