A novel plasma nitriding process utilising HIPIMS discharge for enhanced tribological and barrier properties of medical grade alloy surfaces

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A Novel Plasma Nitriding Process Utilising HIPIMS Discharge for Enhanced Tribological and Barrier Properties of Medical Grade Alloy surfaces

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Abstract

The demand for improvement of lifetime and biocompatibility of medical implants is ever growing. The materials used in this challenging application must display enhanced tribological properties, biocompatibility and reduced metal ion release in long-term clinical performance. Surface modification techniques such as nitriding, can significantly improve the in-service behaviour of the medical grade alloys used for implants. This communication reports on a novel approach for nitriding of CoCrMo alloy using High Power Impulse Magnetron Sputtering, (HIPIMS) discharge for the first time. The new nitriding process has been successfully carried out in an industrial size Hauzer 1000-4 system enabled with HIPIMS technology at the National HIPIMS Technology Centre at Sheffield Hallam University, UK. Due to the significantly enhanced production of molecular (N^{2+}) and atomic Nitrogen (N^{+}) ion species in the HIPIMS discharge, which are primarily responsible for the nitrided layer formation, a fourfold increase in the process productivity as compared to the state of the art nitriding process was achieved. The surface layers produced exhibit excellent mechanical and tribological properties such as high hardness, high fracture toughness and wear resistance. The protection properties of the nitrided layer against corrosion in the aggressive environments of simulated body fluid (Hank’s solution) are remarkably augmented. Furthermore, the data showed that the amount of metal ions released from the HIPIMS nitrided samples was reduced by a factor of 2, 4 and 10 for Co, Cr and Mo ions respectively thus demonstrating the reliable barrier properties of the nitrided layer.

Key words: HIPIMS, Plasma-nitriding, Tribology, Biomaterials

Discussion:

CoCrMo alloys have been widely used for biomedical applications such as knee and hip implants due to their excellent biocompatibility, mechanical and corrosion properties. However, the major drawback of using these alloys is the release of toxic and carcinogenic metal Co and Cr ions because of low resistance to tribo-corrosion and wear. Significant enhancement of the surface hardness, wear resistance and therefore implant lifetime along with minimised metal ion release below the detection limits have been achieved by the application of CrN/NbN nanoscale multilayer coatings deposited by High Power Impulse Magnetron Sputtering (HIPIMS) [1]. In parallel to a coatings approach, researchers are also focusing on enhancing the surface properties of CoCrMo alloys by plasma nitriding. A Conventional Plasma Nitriding (CPN) process utilises a Direct Current (DC) glow discharge, however, suffers from low plasma density and ionised Nitrogen used as a reactive gas.

HIPIMS is a novel pulse power magnetron sputtering technique, which produces highly ionised plasma [2] and was up-scaled for the first time at Sheffield Hallam University, UK by Prof. A. P. Ehiasarian. Conventionally used for coating deposition, it has been found that HIPIMS discharge can be very advantageous to carry out low pressure (pressure (P) typically in the range of 10^{-3} mbar) plasma nitriding (HLPN) compared to standard plasma nitriding (P typically in the range of 10^{-2} mbar) due to the significantly enhanced production of molecular (N^{2+}) and atomic Nitrogen (N^{+}) ion species in the HIPIMS discharge which are primarily responsible for the nitrided layer formation [3]. HLPN has been successfully carried out in an industrial size Hauzer 1000-4 system enabled with HIPIMS technology at the National HIPIMS Technology Centre at Sheffield Hallam University, UK, to plasma nitride samples made from medical grade CrCoMo alloys. The system is equipped with four plasma sources which can be run either in standard magnetron sputtering mode or in HIPIMS mode. Unlike the state of the art plasma nitriding where the ionisation of the working gas nitrogen takes place in a glow discharge sustained between the negatively biased work piece and the chamber walls, the ionisation in the HIPIMS case takes place in the HIPIMS discharge sustained on the magnetrons. To avoid coating deposition, the average HIPIMS power on the magnetrons is kept low so that intensive target sputtering is avoided but the peak power is sufficient for highly ionised plasma to be generated. A high negative bias voltage, (U_b= -900 to -1100 V) is applied to the nitrided components, which attracts the ionised nitriding species and avoids surface coating due to resputtering. The process is carried out at 400° C.

One tangible advantage of the new process is the high nitrogen diffusion rate. Cross-sectional SEM analyses demonstrated that CPN produced a nitrided case depth of 2.1 μm in 18 hours as shown in Fig.1b, whereas the HLPN process produced a case depth of 2.5 μm in 4 hours (Fig. 1a) which represents more than a factor of four increase in process productivity.

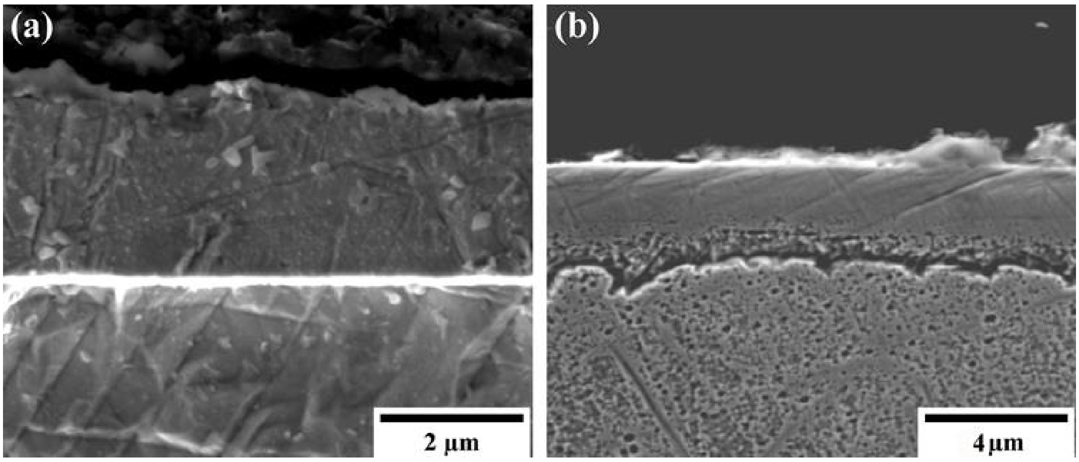

Figure 1: SEM cross-sectional images of the nitrided case produced by (a) HLPN and (b) CPN treatments.

In addition to the enhanced growth rate, nitrogen concentration in the nitrided layer at a control depth of 1.5 μm was a factor of two higher for the HLPN process than the one achieved by the CPN process as confirmed by SIMS chemical depth profile analyses (Fig. 2). The relatively high concentration of nitrogen in the modified layer in combination with other process parameters such as an accelerating bias voltage applied to the substrate allows manipulation of the phase composition in a wide range, extending from a pure S phase (Co_4N or γ_N phase) to a compound layer (Co_4N+$Co_{2-3}N$) as revealed by XRD analyses [4].

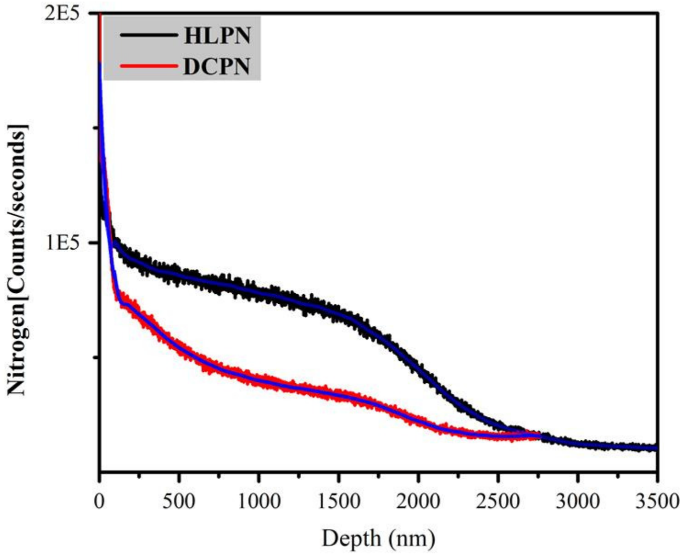

Figure 2: SIMS depth profiles showing Nitrogen content in the nitrided layers.

The HLPN treatment resulted in higher hardness of 23 GPa as compared to 20 GPa achieved for CPN which is substantially higher than that measured for the untreated alloy (7.9 GPa). Consequently, a noticeable improvement in dry sliding wear coefficient for the HLPN treatment was achieved (K_C=1.18×10^{-15} $m^3N^{-1}m^{-1}$) as compared to CPN (K_C= 2.2×10^{-15} $m^3N^{-1}m^{-1}$). The improvement over the untreated specimens, (K_C=6.0×10^{-14} $m^3N^{-1}m^{-1}$) reached almost one order of magnitude higher [5]. Similar enhancement of the tribological performance resulting from the HLPN treatment was evident in the friction coefficient behaviour in dry sliding test conditions. As demonstrated in Fig. 3, the friction curve of the untreated alloy shows a very quick (sliding distance of only 600 m) transition from the run-in state to a high friction coefficient value (μ=1.0) typically associated with catastrophic failure of the material under test. In the following steady state regime the friction coefficient remained high at $\mu=0.82$. In contrast, the friction curve of the HLPN treated alloy is less erratic showing stable low coefficient of friction value of $\mu=0.6$ over the entire sliding distance of 2 km. This study clearly demonstrates the higher quality of the HLPN produced nitrided layer and therefore the advantages of the novel technology.

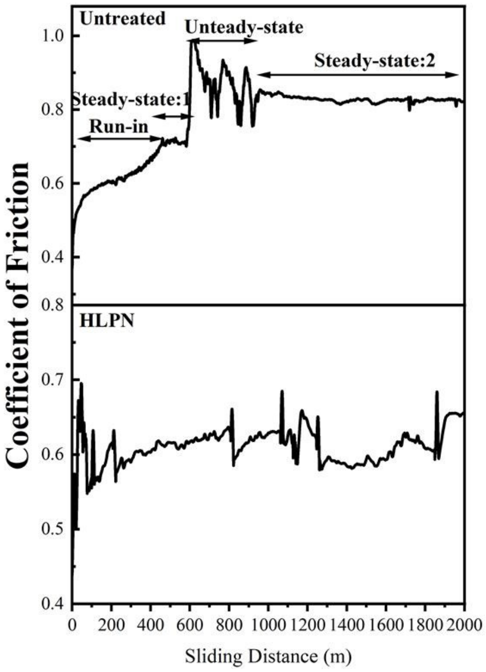

Figure 3: Friction coefficient vs sliding distance in dry sliding conditions: untreated and HLPN treated CoCrMo alloy.

The relatively high values of the hardness-to-elastic modulus ratios H/E and H^3/E^2 of 0.078 and 0.135 respectively defined for the nitrided layers produced by HLPN indicated that the treatment enhances the toughness of the material [6]. This is clearly demonstrated by the SEM images in Fig. 4a-c, which illustrate the crack formation behaviour around the corners and edges of impressions produced by Vickers diamond indentation under a high normal load of 50 kgf on the surface of the untreated CoCrMo alloy and the nitrided layers produced by the HLPN and CPN techniques. Fig. 4a shows that no cracks were developed in the untreated substrate, which is attributed to the ductile nature of the CoCrMo alloy. Fig.4b shows that the area around the corner of the impression for the HLPN layer despite the plastic deformation evidenced by the presence of shear bands is crack free demonstrating the higher layer toughness. In contrast, the CPN layer exhibits a high crack density, which is typical of brittle materials Fig. 4c.

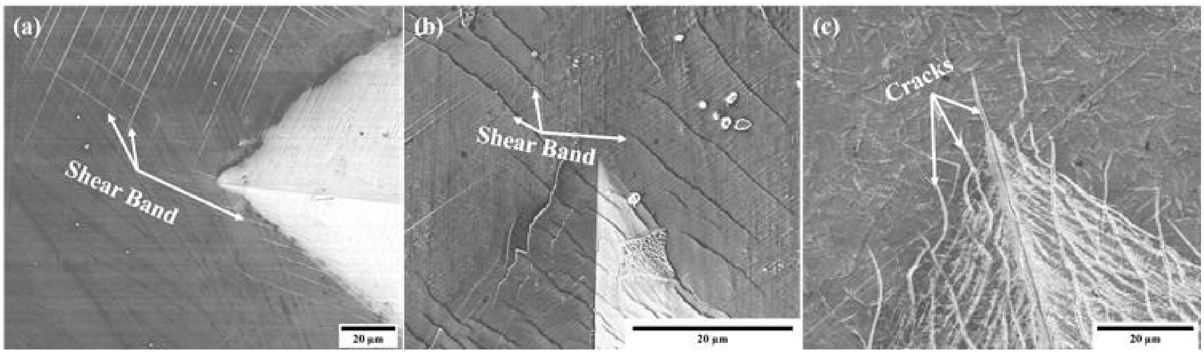

Figure 4: SEM images of Vickers diamond indenter impressions (50 kgf load): (a) untreated CoCrMo alloy, (b) HLPN treated (c) CPN treated.

Potentiodynamic polarisation tests in Hank's solution (simulated body fluid) showed a significant improvement in corrosion resistance of the HLPN-treated alloy whose corrosion potential, E_{Corr}= -218 mV, was considerably nobler compared to the untreated alloy (E_{Corr} = -775 mV). Similarly, the corrosion current densities measured for the HLPN nitrided alloy of (ICorr = 5×10^{-5} $mAcm^{-2}$) were found to be two orders of magnitude lower than the untreated CoCrMo alloy (ICorr = 2×10^{-3} $mAcm^{-2}$). Metal ion concentrations released from the samples in a Hank's solution electrolyte (pH:7.3) were determined by ICP-MS analysis. The data showed that the amount of metal ions released from the HLPN treated samples was reduced by factor of 2, 4 and 10 for Co, Cr and Mo ions respectively. The analyses showed clearly that the new HLPN treatment produces layers which are a reliable barrier against metal ion release from CoCrMo alloys.

Conclusions:

- A novel plasma nitriding process utilising HIPIMS discharge has been successfully developed first time allowing fourfold increase in the process productivity as compared to the state of the art nitriding technology.
- The surface layers produced by the new technique exhibit excellent enhanced mechanical and tribological properties such as high hardness, high fracture toughness and wear resistance.
- The new HLPN treatment produces layers with augmented barrier properties such as high corrosion resistance which effectively hinder Co, Cr and Mo metal ion release in simulated body fluid, (Hank's solution).
- The enhanced mechanical, tribological and corrosion resistance properties and favourable Me-ion release performance makes the novel HIPIMS enabled plasma nitriding a powerful technique for surface treatment of medical-grade alloys.

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Figure captions

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Figure 2: SIMS depth profiles showing the Nitrogen content in the nitrided layers.

Figure 3: Coefficient of friction vs sliding distance in dry sliding: untreated and HLPN treated CoCrMo alloy.

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