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# Comparison of the structural and corrosion properties of the graphene/ $SiN_{(200)}$ coating system deposited on titanium alloy surfaces covered with SiN transition layers



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#### ABSTRACT

In this paper, comparative studies of the structural and corrosion properties of SiN/graphene/SiN coating systems with various SiN transition layer thickness have been investigated. The coating systems were formed on Ti6Al4V alloy surfaces. The SiN transition layer thicknesses varied from 100 nm to 300 nm. The thickness of the upper silicon nitride thin film, in all examined cases, was 200 nm. The silicon nitride thin film was deposited using the Plasma Enhanced Chemical Vapour Deposition method. A graphene monolayer was transferred onto the silicon nitride surface using the "PMMA-mediated" method.

The structural characteristics of coating systems obtained were examined using Raman spectroscopy, optical profilometry and SEM measurements. The corrosion properties of the coating systems were determined by an analysis of the voltammetric curves.

The SiN/graphene/SiN coating system with a 300 nm thick silicon nitride transition layer is characterised by the best structural and corrosion properties of all tested coating systems. In this case, the surface of the top silicon nitride thin film has no holes or flakes, as opposed to the coating systems with 100 nm and 200 nm thick transition layers, in which the upper SiN thin film flaked and dropped off. The value of corrosion current density obtained for this sample was almost two orders of magnitude lower than the current density obtained for the other tested coating systems.

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#### 1. Introduction

Titanium alloys have many potential industrial applications, mainly owing to their good mechanical and corrosion properties and biocompatibility [1–3]. However, some of these applications are limited because of certain unsatisfactory surface parameters, i.e. low hardness, low wear resistance and low corrosion resistance in hot, concentrated and low - pH solutions [4–7]. To bypass these obstacles, many various surface treatment techniques are used. These methods include, burnishing and surface micro-shot peening and thermo-chemical treatment, in particular based on the PVD and CVD methods [8–11]. Another way to protect titanium alloys and improve their surface properties is the application of ceramic coatings, i.e. silicon nitride. Silicon nitride thin films can be described as materials with high density, low wear rates, good insulating properties, excellent Na<sup>+</sup> resistance, relatively high fracture toughness, strength, high temperature corrosion resistance in an

\* Corresponding author. E-mail address: malgorzata.kalisz@its.waw.pl (M. Kalisz). oxidizing atmosphere and in a sulphidizing-oxidizing atmosphere [12] and excellent biocompatibility [13–15]. They are an excellent diffusion barrier against water and aggressive contaminants that can corrode titanium alloys [16]. Silicon nitride films can be deposited by low-pressurechemical-vapour-deposition (LPCVD), plasma enhanced chemical vapour deposition (PECVD) and reactive radio frequency (r.f.) sputtering techniques, but their structural, mechanical and corrosion properties highly depend on the technological process used [17–19].

Graphene has already proven to be an alternative way to improve the surface properties of titanium alloys, especially corrosion resistance. Recent studies have shown that a single graphene layer considerably increases the corrosion resistance of materials such as copper [20], nickel [21] and titanium alloy [22] and protects the surface of those metals from oxidation [22]. Unfortunately, a single layer of graphene does not change the mechanical properties of the surface on which it is deposited [22].

Previous research has shown that a combination of two types of coatings, such as silicon nitride and graphene monolayer, in a hybrid coating system, having a thickness of several hundred nanometres, is