# COMPARISON OF SILVER AND COPPER AS DOPANTS OF CARBON COATINGS


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## Introduction

Scientists and doctors from around the world are constantly trying to find solutions to emerging problems associated with the use of implants, despite the noticeable process of improving currently used materials and introducing new ones. Still problematic are biological effects such as: release of metal ions from the implant or wear products into surrounding tissues, cytotoxicity and genotoxicity, but also formation of biofilm layers which may lead to severe inflammations.

Since initial and long-term behaviour to the implanted material depends largely on its surface interactions with the body, high impact is placed on approaches involving various types of coatings such as structures of $TiO_2$ [1] or diamond like carbon (DLC) coatings [2]. Further improvement of desired features can be achieved by doping of such films. There are at least a dozen different admixtures of only DLC coatings reported by literature [3,4]. Among the elements of high bactericidal potential but still unsure effect on mammalian cells are copper and silver. The purpose of the following researches was to compare and contrast the effect of Cu and Ag as dopants of DLC coatings in potential biomedical applications such as coatings for intramedullary nails.

## Materials and Methods

AISI 316 LVM was selected as a substrate material for all the coatings taking into consideration its wide use as a material for implants. Both Cu-DLC and Ag-DLC coatings were deposited by means of PVD process in which carbon matrix was originated from graphite source while dopant was introduced via sputtering of metal target.

The chemical composition of examined coatings was verified by means of X-ray photoelectron spectroscopy (XPS) examination conducted with AXIS Ultra DLD (Kratos Analytical) system and Raman spectroscopy performed with help of InVia (Renishaw) apparatus. Mechanical properties were evaluated using Nano Indenter G200 (Agilent Technologies, USA).

During evaluation of the bactericidal effect of Ag and Cu, the liquid culture of model organism *Escherichia coli* was used. The number of bacteria adhered to the examined surfaces was determined by means of fluorescent spectroscopy of specimens treated with propidium iodide and bis-benzamidine.

## Results and Discussion

Initial trials of radio frequency magnetron sputtering of Cu and Ag targets with powers from 5 to 25 W were associated with a significant reduction of the hardness of the deposited coatings in relation to undoped DLC. In most cases, the hardness of coatings was on a similar or lower level than the one observed for substrate material. Also the results presented by other research groups showed depletion of hardness especially with addition of silver [5]. Probably those coatings were in fact composites of metal with only a small addition of carbon, similar to the coatings produced by Khamseh et al. [6]. The satisfactory hardness (resembling value of DLC) was achieved by introducing screens that limit the effective sputtering surface of the dopants' targets. Finally the coatings with amount of Cu of up to 7 at.% and Ag of up to 10 at.% were synthetized. Some reduction of hardness with high amounts of dopants was related with increasing fraction of bonds with sp2 hybridization.

The biological examination revealed a reduction of the number of adhered bacteria on both Ag-DLC and Cu-DLC but only at certain level of dopant. In literature, a significant reduction of biofilm formation was achieved at amounts of copper of at least 9 at.% [7], which is higher than maximum amount of that dopant examined in the following work. The bactericidal potential of coatings with silver was higher than in case of addition of Cu to the carbon matrix, which is in agreement with the results of Goudouri et al. [8] conducted for metals.

## Conclusions

Conducted researches prove the possibility to deposit Cu-DLC and Ag-DLC coatings with hardness not lower than for substrate material and for low amounts of dopant resembling even the value for undoped coating. Both tested dopants elements can reduce biofilm formation, but the bactericidal effect is dependent on the type of dopant and its concentration.


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