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# Functional properties of ceramic-Ag nanocomposite coatings produced by magnetron sputtering



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#### ABSTRACT

In recent years, the use of nanocomposite materials to functionalize surfaces has been investigated, taking advantage of the complementary properties of the nanocomposite constituents. Among this family of materials, ceramic-Ag coatings have been widely studied due to the large variety of functionalities that silver possesses and the possibility of tuning the coating's practical features by selecting the proper matrix to support this noble metal. Therefore, this review focuses on the effects of silver nanoparticles on the functional properties of ceramic-Ag nanocomposites. The chemistry, structure, morphology and topography of the coatings are analyzed with respect to the changes produced by the silver nanoparticles' distribution, amount and sizes and by altering production process variables. To offer a clear understanding of the functionalities of these materials, the optical, electrical, mechanical, tribological, electrochemical and biological properties reported in the last decade are reviewed, focusing on the ability to tune such properties by modifying the silver distribution, morphology and composition. In particular, the surface plasmon resonance, self-lubricating ability and antibacterial effect of silver are covered in detail, establishing their correlation with factors such as silver diffusion, segregation and ionization.

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#### 1. Introduction

Ceramic-Ag coatings are part of a large collection of protective and functional coatings used to modify the properties of the base material. In these coatings, ceramic phases such as oxides, carbides, nitrides and carbonitrides are mixed with metallic silver to enhance the functionality of the system. These coatings have attracted a considerable amount of attention due to their large range of applications. Their multi-phase character confers independent characteristics from each immiscible phase (ceramic or metallic) in the system, providing multiple functional properties, including antibacterial effects [1–22] wear resistance [2,4,23–37], corrosion resistance [18,29,38–42] and light absorption enhancement [43–52], among others. One of the most interesting features of these materials is the possibility of tailoring their functionality by selecting the appropriate type, distribution and size of the constituent phases.

A large number of techniques have been used to produce ceramic-Ag coatings, including electrochemical methods, physical vapor deposition (PVD) (e.g., [53]), chemical vapor deposition (CVD) (e.g., [54]) and sol-gel (e.g., [55]) techniques. However, to produce a detailed review of ceramic films with embedded silver nanoparticles and their effect on the coatings' properties, the present review focuses on coatings consisting of silver nanoparticles in ceramic matrices deposited by magnetron sputtering (MS), one of the most commonly used physical vapor deposition techniques. In fact, the diversity of properties exhibited by this group of materials is mainly dominated by the diffusion and growth of the silver nanoparticles in the matrix and the structural nature and the morphological characteristics of the coatings, which are therefore a fundamental factor in the coatings' behavior. These characteristics are strongly affected by the production conditions, resulting in a myriad of outcomes, which is why this review is limited to the MS technique.

#### 2. Magnetron sputtering

MS is a deposition technique belonging to a large group of sputtering processes included among PVD technologies. Briefly, for the sputtering process, an electric field is created between two plates (electrodes) within a vacuum chamber. A non-reactive gas (usually Ar) is injected into the chamber, is positively ionized due to the electric field and bombards the negative pole of the electric field, the cathode of the discharge. The collisions of Ar<sup>+</sup> ions with the material located in the cathode, known as the target, cause the ejection of atoms/molecules from the surface toward the substrates [56].

The ionization and collision rates of argon in sputtering systems are generally low, resulting in very slow deposition rates and poor film densities. Thus, a variation of the sputtering technique was introduced in 1930 [57] to increase the ionization rate in the vicinity of the target and increase the deposition rate of the films. This modification, MS, consists of a set of magnets placed beneath the target, which provide a magnetic field to trap the secondary electrons emitted by the target into the discharge, increasing the ionization of argon around the target and, consequently, increasing the target bombardment. All of these components are schematized in Fig. 1a.

MS can be either unbalanced or balanced, which refers to the magnitude of the magnetic field between the poles of the magnets that form the magnetron. Balanced magnetrons possess the same strength in terms of the magnetic field between the south and north poles of the magnet, generating closed field lines between these poles [58]. In the unbalanced mode, by contrast, the strengthened magnetic field in the poles in the exterior of the magnetron allows the magnetic field lines to be directed toward the substrate. These two types of magnetrons are schematized in Fig. 1b.

In addition to magnetic field balancing, the film features can be modified by altering several parameters in the production process, such as the number of magnetrons, the type of power supply, the current density, the distance between the magnetron and the substrate, the pressure in the chamber (known as the discharge pressure) and the temperature of the

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