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Low-pressure plasma treatments for cleaning metallic heritage artefacts

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# Summary

Restoration and conservation of Cultural heritage is a multidisciplinary field that takes advantage of engineering and material science for developing tailored strategies for long-lasting conservation by means of innovative and reversible materials for restoration, non-invasive analytical techniques. Cleaning Metallic artefacts is a primary step in the restoration and conservation processes. For this reason Low-pressure Plasma is proposed as an effective and environmentally friendly technique for cleaning different materials such as metals artefacts. Moreover, strategies for preventive conservation have to be considered as next step. The metallic artefacts are sensitive to the atmospheric corrosion in indoor environments as museum. A new smart monitoring system to assess the environmental conditions and the atmosphere aggressiveness in a museum indoor environment has been developed and tested. The main objectives of this thesis are to examine the efficiency of the plasma for cleaning metallic artefacts and to test a new real-time monitoring system. The thesis consists of five chapters: Chapter 1 deals with the state of the art of low-pressure plasma in the field of cleaning and protecting metallic artefacts. Chapter 2 deals with an experimental study on plasma cleaning of copper and silver samples aged by electrochemical treatment for copper-based alloys and tarnished by  $H_2S$  exposure for silver samples. Several parameters in plasma cleaning using hydrogen and argon were modified in order to optimize the procedure. Plasma cleaning shows a higher efficacy silver-based alloy samples than on copper-based alloys. Chapter 3 is a study of the corrosion mechanisms of copper-based alloys and Silver based alloys. A case study is considered, the characterization of some ancient coins found in an excavation site in AL-Fustat in Egypt, with a deeping on interaction between the soil and the corrosion products and the production methods of the artefacts. The analytical techniques employed were FESEM coupled with EDS, optical microscopy, XRD. The results showed that all the coins were made of bronze with variable amounts of tin. The production method was hammering into molds. Moreover, the corrosion products were copper oxides and copper chloride due to long-term burial period in a soil which is rich in chloride ions. Chapter 4 is a study of the indoor environment aggressivity by means of the smart sensors environmental monitoring system and of a set of reference samples, constituted by copper specimens coated with nano-structured thin film. Chapter 5 deals with

the environmental monitoring system , based on a wireless network composed of small sensors, designed to satisfy the requirements for their employment in the Cultural Heritage field. The sensors are stand-alone devices able to measure temperature and relative humidity for three years, connected through a wireless link to a small receiver for routing data to a cloud system. The proposed system contains a set of copper reference specimens coated with a Cu nano-structured films deposited by plasma sputtering to be located close to the sensors to assess the atmosphere aggressiveness. A monitoring campaign was performed for one year in the museum of the Faculty of Archaeology at Sohag University in Egypt and allowed to obtain a map of the climatic conditions in the museum and to develop strategies for improving the stability of the environmental conditions. Furthermore, from a material science point of view, the higher sensitivity of the Cu-nano-structure thin film to the atmosphere with respect to bulk copper, due to the increase of the number of the grain boundaries, allows to proposed them as proper reference materials . Moreover an artificial ageing of copper specimens coated with nano-structured thin film following the ISO 3231-1993 standard method for the determination of resistance to humid atmospheres containing sulphur dioxide was performed.