Mechanistic insight into the impact of induction heating on the morphology and crystallinity of copper particles electrodeposited on nickel

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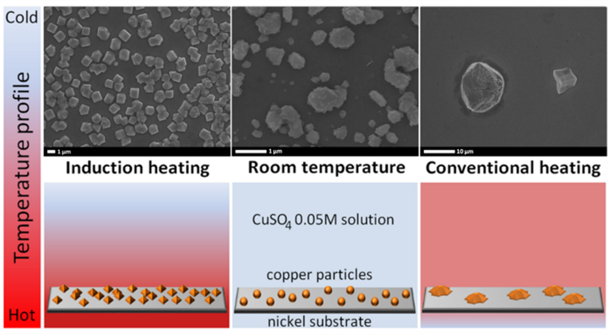

Copper and its oxides are very versatile materials used in many applications such as microelectronics, catalysis, gas sensing, *etc.*
Structural characteristics of nanoparticles (NPs) can be adjusted to improve their properties. Among the solution-based chemical methods for the synthesis of Cu NPs of well-defined shape and size, two main approaches are considered: the use of a template and the addition of capping agent.[1] However, the presence of template material and/or capping agents at the surface of the formed NPs may have undesirable effects for some applications.
Electrochemical deposition parameters are also known to influence the morphology and crystallinity of the obtained deposits.[2-4] Among these parameters, temperature and its gradient is also known to play a significant role on the electrodeposition kinetics[5,6] and the resulting deposit morphology.[5-8] Mass transport is enhanced by establishing thermal convection and increasing the diffusion coefficient while the electrode heating accelerates sluggish reactions kinetics[6] and a difference in the growth rate of the limiting planes causes specific facets to be exposed.[9] Changing the kinetic conditions by heating the system can thus be used to change the final shape of the formed particles.[10] Furthermore, A. Milchev *et al.* have shown that the growth kinetics of copper crystals on glassy carbon surface is determined by combined charge transfer and diffusion limitations under potentiostatic conditions.[11-13] A mass transport enhancement such as the one obtained in electrochemical systems with heated electrodes can therefore be expected to greatly influence the growth kinetics regarding the diffusion limitation aspects.
We have shown this in two previously published exploratory studies.[14,15] In these works, we reported on the study of copper galvanostatic electrodeposition on nickel substrates and the comparative effects of a conventional heating (CH) of the solution (isothermal situation) and an induction heating (IH) of the nickel substrate (non-isothermal situation) on copper particles morphology. It has been shown that in temperature-equivalent conditions, CH leads to a low coverage of the nickel electrode with weakly adherent copper microparticles (with a very large size distribution) whose growth could be subjected to a mass-diffusion limitation while IH leads to a high coverage of the surface with well adherent and highly crystalline Cu NPs (with a sharp unimodal size repartition) avoiding any diffusion limitation.
The objective of the present work is to further investigate the mechanistic aspects of the galvanostatic Cu particles electrodeposition on Ni under IH by means of *in situ* potential and surface temperature measurements correlated with SEM observations of the deposited Cu particles. We show that in the applied conditions (i = - 2 mA/cm² in a $CuSO_4$ 50mM aqueous solution at pH 3), the heating method has a significant influence on the deposit morphology as well as on the resulting overpotential.
A CH of the bath at 60 °C leads to a significant increase of the overpotential value from 0.11 to 0.16 V while the application of IH during the electrodeposition increases the overpotential value up to 0.18 V. When IH is stopped, this overpotential value decreases back to a value close to the one measured for electrodepositions at room temperature. The highly crystalline morphology of the Cu particles obtained with IH (despite the important overpotential) has been explained by IH induced convection phenomena (i.e. the decrease to some extent of the hydrogen evolution reaction by decreasing the proton concentration at the electrode-solution interface and the increase of the speed at which the formed hydrogen bubbles are removed from the surface allowing the formation of smooth a well-developed copper crystalline faces). Moreover, convection allows avoiding Cu ions depleting at the Ni surface and therefore prevents diffusion limitation phenomena, allowing the formation of well-defined Cu crystals without branching.
Induction heating appears as a convenient tool for an easy control of the morphology and crystallinity of electrodeposited copper particles without any additives.

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