Ag / Cu (001) electrodeposition: a comparison between Kinetic Monte Carlo simulations and the Cluster Nucleation Theory.

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It is well-known that interactions between adsorbate atoms have a large influence on the electrode response during electrodeposition [1]. We consider here the case of attractive interactions illustrated by the deposit of Ag on a Cu (001) electrode. We use equilibrium and kinetic effective Ising models, whose parameters are derived from an N-body interatomic potential issued from the second-moment approximation of the tight-binding scheme [2]. This allows us to take into account the influence of the atomic relaxations on the adsorption energy and on the pair interactions between the deposited Ag atoms, while keeping a lattice-gas formalism [2].

The same lattice-gas model is used to perform Monte Carlo (MC) simulations and to derive analytical solutions within the mean-field approximation (MFA). The drawback of this last approach is to neglect the influence of the microstructure (clusters of atoms or aggregates of vacancies) on the kinetics of electrosorption.

As expected, at sufficiently high temperatures, the Monte Carlo isotherms are in perfect agreement with the isotherms obtained within the mean field approximation, due to the absence of local correlations between adsorbates. At lower temperatures, the attractive interactions among the adsorbates leads to a first-order phase transition. The critical electrochemical potential for the Monte Carlo isotherms is located at the same value as the one obtained with MFA, but the width of the hysteresis cycle is strongly reduced. Actually, the hysteresis is related to a nucleation process in Monte Carlo simulations. Such process is not taken into account in MFA, which can only describe homogeneous instabilities.

We then study the kinetics of adsorption, following a sudden potential step. The system is initially prepared at a potential μ_i sufficiently low to correspond to $c_0 \approx 0$, where c_0 denotes the concentration of Ag atoms. The potential is suddenly increased to a new value, μ_f, and kinetic simulations (Monte Carlo and MFA) allow us to obtain the time evolution of the coverage. We consider a final value of the potential slightly outside the hysteresis of the MC isotherm. The MC kinetics is slower than the MFA kinetics by one order of magnitude (fig.1). Monte Carlo kinetics is dominated by nucleation and growth processes and is well described by the Kolmogorov-Avrami (KA) equation [3]:

$$c_0(t) = c_0^{eq} (1 - \exp(- k_{KA} (t + \tau)^3))$$

This formalism takes into account the nucleation exclusion zone appearing and spreading around each growing nucleus and their overlap (fig. 2). τ is the incubation time, and k_{KA} is a constant which depends on the nucleation rate and on the growth rate of the clusters [4]. The MFA homogeneous model, which cannot describe the formation and the growth of the clusters, is no more valid, and must be replaced by the phenomenological KA formalism.

The use of the classical nucleation theory (CNT) allows us to express k_{KA} as a function of the energetic parameters of the kinetic Ising model. However, we observe very large deviations between the CNT and Monte Carlo simulations concerning the nucleation rate and the growth rate of the clusters. By incorporating carefully the configurational entropy of the clusters and the morphology of the edge of these clusters (in particular, the number of kinks) in the CNT equations, we recover an excellent agreement between MC simulations and this modified CNT-KA approach.

This work illustrates the efficiency of mixing atomistic simulations as Monte Carlo simulations with mesoscopic modeling, such as the CNT-KA approach.

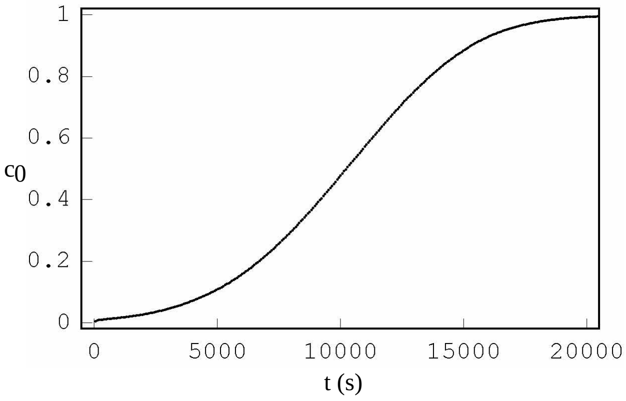

Fig. 1 : MC kinetics following a potential step with μ_f = - 3.04 eV, starting from $c_0(t=0) \approx 0$.

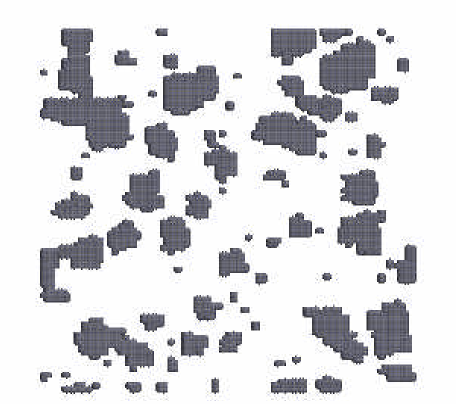

Fig.2 : Snapshot of the atomic microstructure of the adlayer obtained by MC simulations when $c_0 \approx 0.25$ for μ_f = - 3.04 eV.

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