# Electrochemical investigations of the relationship between grain size and corrosion processes in nanocrystalline grain size range

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## Introduction

Understanding of how grain size affects the corrosion processes has not been actually achieved [1]. Despite the large interest on the nanocrystalline materials and their unique properties, the superior corrosion resistance of lower grain size is not clearly established and stays a controversial subject. As corrosion resistance can be affected by several metallurgical parameters (defects, grain size, grain-boundary, purity, crystallographic texture, roughness …), a careful control of the microstructure of the materials is necessary which is not the case for many studied reported in the literature. The aim of this work is to acquire a better knowledge of the interplay between microstructure, composition, and corrosion resistance. To carry through these objectives, nanocrystalline nickel was chosen as a model material. Nickel coatings with grain sizes ranging from 40 nm to several micrometers were obtained by DC and pulse electrodeposition in a sulphamate bath without additive, in order to minimize sulphur incorporation. The composition of the coatings was analyzed and different tools were used to carefully characterize the coating structure at different scales. Polarization curves (in $H_2SO_4$ 1M) were used to study the anodic behaviour and the kinetics of the Hydrogen Evolution Reaction.

## Experimental

The material used in this study is nickel with different chemical and metallurgical states. Nanocrystalline coatings were obtained by electrodeposition and their behaviour was compared with reference samples: 99.89% commercial non textured nanocrystalline sample (nano GF) with a nominal grain size of 20 nm, 99,57 % non textured polycristal with a grain size of 168 μm, and 99.99% single crystals (100) and (110) provided by Goodfellow Company. For each sample, chemical and microstructural characterizations were conducted using a large number of techniques (GDOES, SIMS, SEM, XRD, TEM, EBSD, AFM). Corrosion behaviour (anodic and cathodic reactivity) was studied in dearated $H_2SO_4$ 1M bath at 300K with a special attention given to the surface preparation before electrochemical test.

## Results and Discussion

For the grain size explored (40 nm to 1 μm), three kinds of textures: <100>, <110> and random distribution (rd) were obtained depending on electrodeposition conditions. Coincidence Site Lattice (CSL) and disorientation angle have been classically used to distinguish the nature of grain boundaries. High-angle grain boundaries (HAGB) are characterized by a disorientation angle above 15°. Grain boundaries can also been qualified by $\Sigma$ parameter that denotes the fraction of atoms in the grain boundary plane which are coincident to both lattices. Low coincidence site lattice grain boundaries are characterized by a high $\Sigma$ value ($\Sigma > 29$) and are mentioned as HCSL. These parameters were evaluated by using EBSD. An increase of the fraction of high disorientation angle (HAGB) is observed as grain size decreases (figure 1a). The amount of coincidence site lattice (CSL) is also strongly modified, showing an increase of the abundance of HCSL when grain size decreases (figure 1b). Both results show that dislocation density and disorder (and then vacancies content) in grain boundaries increase as grain size is reduced. Concentration profiles and cartographies were obtained for each atomic element, showing that the impurities were homogeneously distributed laterally and through the thickness of the coatings. For deposits with high grain sizes, which are associated with a marked <100> texture, the amounts of solutes are very low, reaching values around 99.99%. However, for the coatings with a lower grain size the contamination drastically increases especially for interstitial elements (H, O, C) and for some substitutional solutes (Cl and Cu). The total amount of interstitial impurities (resp. substitutional impurities) reaches 1500 ppm wt (resp. 1750 ppm) for the lowest grain sizes. This increase can be correlated with a higher disorder in grain boundaries (increase of HCSL) when grain size is decreased (figure 1b).

The consequence of the evolution of grain size, grain boundaries characteristics and solute content on corrosion kinetics is questioned with electrochemical polarization curves recorded using steady state voltametry (0.5 mV/s scan rate). All theses curves were simulated using classical HER cathodic model [see as example 2,3] and anodic dissolution model [see as example 4,5]. The kinetic constants obtained by this approach relate the rate of the different electrochemical steps, which occur during the adsorption of hydrogen (only Volmer process is presented in present paper) $k_V$, or during the adsorption of of the dissolution intermediaries species:: respectively $OH^-$ ($k_1$) and $HSO_4^-$ ($k_5$) and during the transfer of activated complexes: respectively $NiOH_{ads}$ and $\left(NiHSO_4\right)_{ads}$. The kinetic constants obtained for the different nanocrystals was normalized by the ones obtained for single crystals with the same "texture" (100 and 110 orientations) or for non-textured polycrystal with a large grain size (NT) (figure 2). The reduction of grain size has the same consequence on the adsorption steps (figure 2a, 2b, 2c). The increase of the fraction of grain boundaries with high misorientation (HAGB) when the grain size decreased reduces the adsorption activity. In opposite solute content at low grain size seems to promote the adsorptions steps. Figures 2d and 2e illustrate the fact that the transfer of activated complexes is promoted by the large fraction of grain boundaries (the ratio is higher than 1). Despite the results, we observed that the activation process is lowered when the fraction of grain boundaries with high misorientation increases.

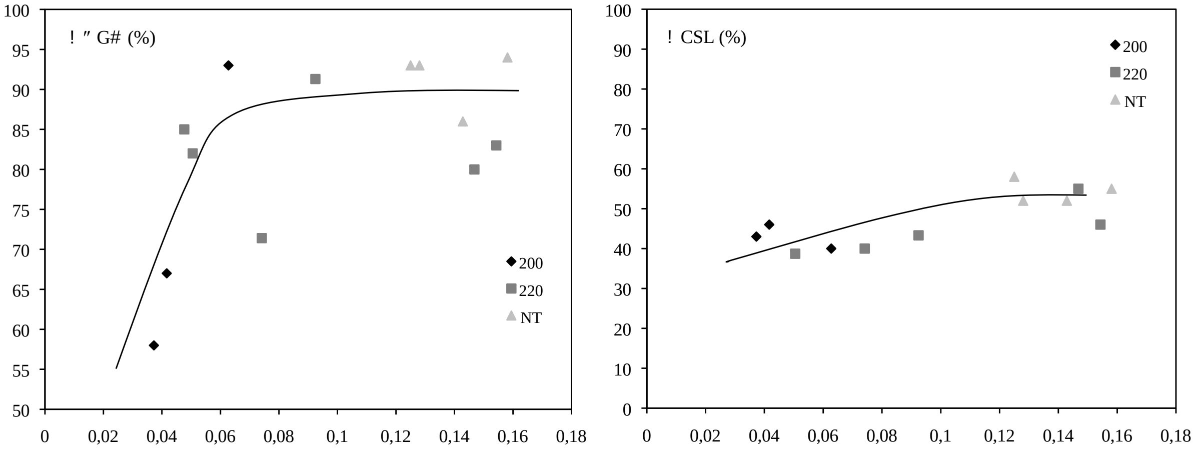

Figure 1: Evolution of HAGB fraction (a) and HCSL fraction (b) *versus* the inverse of the scare root of grain size.

## Conclusions

Nanocrystalline nickel is actually the subject extensive investigations, especially to increase corrosion resistance. As corrosion resistance can be affected by several metallurgical parameters (defects, grain size, grain-boundary, purity, crystallographic texture, roughness …), a careful control of the microstructure of the materials is necessary. In the present work, the competition effect between solute content and dislocation density in grain boundary on cathodic and anodic processes is illustrated.

## Acknowledgements

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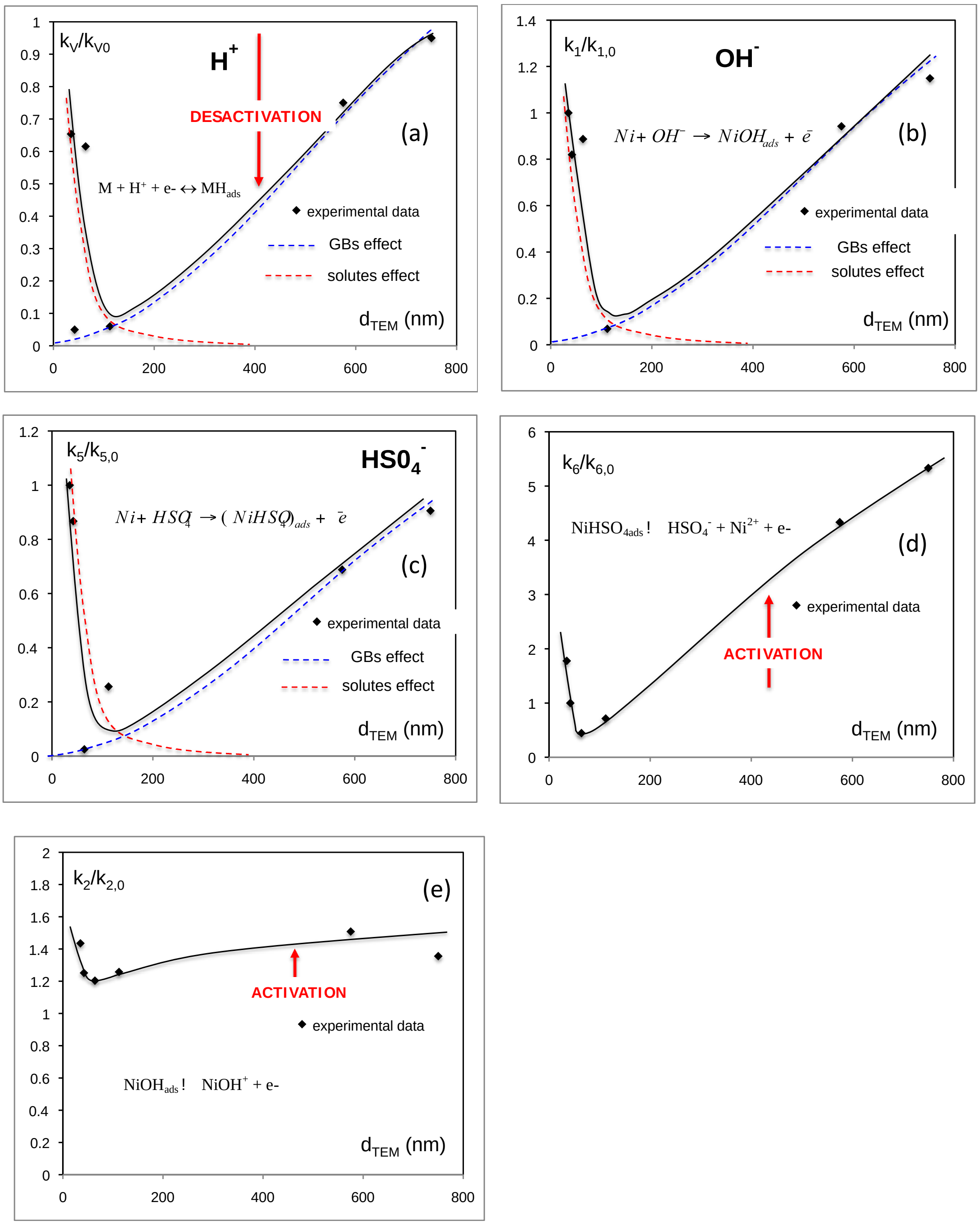

Figure 2: Evolution of the kinetic constants associated with the different electrochemical steps of corrosion processes.