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Interface structure of Ni nanoparticles on MgO (100): A combined HRTEM and molecular dynamic study

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Abstract

Ni clusters with an average size of 4 nm, supported on MgO micro-cubes were studied by high resolution electron microscopy (HRTEM) and image simulations by the multislice technique. Regular defects were evidenced in the metal clusters at the interface. Molecular dynamic calculations of a 4 nm cluster indicates the same type of defects. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The physical and chemical properties of supported metal clusters can be modified by the interactions with the substrate and by the structural variations due to their limited size [1,2].

Many high resolution transmission electron microscopy (HRTEM) studies were performed for the determination of the atomic structure and the formation of intermediate compounds in the metal–ceramic interfaces [3]. The interface structure of bulk Cu on Al₂O₃ was determined for a thick Cu film (1 μ m) on a sapphire (0001) single crystal [4] and for an Ag bulk layer on MgO [5]. The same technique was used in the case of Cu clusters larger than 10 nm, embedded in a Al₂O₃ matrix [6], and for nanoparticles supported on various oxides, as Pd/MgO [7], Pd/ZnO [8], Au/MgO [9], PdCu/MgO [10] and Au/TiO₂ [11]. Most of these interfaces are non reactive, and some of them (Ag/MgO (100) and Pd/MgO have been observed in situ by grazing incidence X-ray scattering. By this technique, in

the particular case of Ni layers grown on MgO single crystals, a complex structure was evidenced by using surface diffraction [12].

For reactions of hydrogenation, the catalytic activity and selectivity of Ni nanoparticles supported on MgO were found higher than in the commercial Ni catalysts [13].

The comparative studies of the Ni catalytic activities for CH_4 reforming, on different substrates as MgO, TiO₂, Al_2O_3 , show that the Ni clusters properties strongly depend on the metal support interactions [14].

The recent interest for supported Ni clusters is mainly due to their catalytic properties for the carbon nanotubes production [15].

Here, the interface Ni/MgO is studied at the atomic scale by HRTEM, associated to image analysis and image simulations by the multislice technique and molecular dynamic simulations.

2. Preparation technique

Pure Ni particles were prepared by the decomposition of $Ni(acac)_2$ on MgO oxide powders. The $Ni(acac)_2$ (Fluka), from 40 to 90 mg, was dissolved in acetonitrile (200 ml). MgO (Fluka) clean powders (200 mg) with a surface

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Fig. 1. TEM image of Ni clusters on a MgO cube: an overview.

specific area of 30 m² g⁻¹ were mixed in the solution and stirred at 80 °C until complete evaporation of the solvent. After drying at 80 °C in air, the powders were slowly annealed in vacuum (10⁻⁴ mbar), until 450 °C, then reduced under H₂ at 400 mbar during 3 h at the same temperature [16,17].

The powders were dispersed on a copper grid covered with a carbon film and observed in standard electron microscopy, with a Jeol 2000 FX microscope. The metal particles seen in Fig. 1 have nanometer size distribution $(3.5 \text{ nm}, \pm 1 \text{ nm})$.

3. HRTEM observation

The preparations were observed with a Jeol 3010 microscope for high resolution imaging (300 KV, $C_s = 0.6$ mm).

In Fig. 2a, a Ni cluster is seen in profile view along a [100] direction. The shape is limited by two [011] edges. At the interface, in the two first metal layers, three defects

1 nm

Fig. 2a. HRTEM image of a Ni cluster in profile view, supported on MgO. In inset is the Power Spectrum showing the splitting of the 200 spots from Ni and from MgO.

can be seen with a periodicity of 1.24 nm. Below the clusters, some moiré fringes in the substrate were attributed to local deformations in MgO. In the power spectrum in inset, the (200) reflexions are splitted, and correspond to the d_{200} distance of bulk MgO and bulk Ni.

By numerical analysis of the image [18], the intensity profiles were recorded along the [100] direction parallel to the interface. The average distance between the (200) fringes is plotted in Fig. 2b as a function of the Ni layer number from the interface. The two first layers at the interface, which contain the defects, are disturbed, then the lattice corresponds to bulk Ni.

The structure and defects at the interface were enhanced by Fourier filtering [19,20]. In Fig. 2c, three dislocations are seen with an average distance of 1.25 nm. This distance



Fig. 2b. Average distance between the (200) lattice planes normal to the interface in Ni, from the interface to the top of the cluster.



Fig. 2c. Fourier filtered image of Fig. 2a with the 020 reflexions. Three dislocations are indicated by arrows.

corresponds to the superimposition of seven unit cells of Ni on six unit cells of MgO.

In Fig. 3, a Ni cluster is seen in top view on the substrate. Two sets of moiré fringes are parallel to the [100] and [010] directions, with a periodicity of about 1 nm. In the corresponding power spectrum, the satellites due to the moiré fringes are seen around the (200) spots. The superimposition of the (200) lattice fringes of bulk Ni $(d_{200} = 0.176 \text{ nm})$ and bulk MgO $(d_{200} = 0.21 \text{ nm})$ gives moiré fringes with a calculated distance D = 1.08 nm, which is the distance measured in the experimental images.

Furthermore, the superimposition of Ni layers on varying thickness of MgO were simulated by the multislice technique with the EMS program [21]. The supercells with Ni, and MgO were built with the dimensions 2.1×2.1 nm² which corresponds to the superimposition of 6×6 unit cells of Ni on 5×5 unit cells of MgO. In the images (Fig. 4a, b), the moiré fringes loose contrast as the thickness of the substrate increases. The moiré fringes are no longer visible for



Fig. 3. HRTEM image of a Ni cluster (001) oriented on MgO, in top view. The power spectrum in inset shows the satellite reflections around the central spot and the 200 spots, due to the moiré fringes.

a 2.1 nm thick Ni layer (12 ML), which is about the height of the cluster in Fig. 2, in epitaxy on a 63 nm thick MgO layer (30 ML).

4. Molecular dynamics calculations

Prediction of the atomic structure can be performed by quenched molecular dynamics simulations using semiempirical potentials as done recently on the Pd/MgO (100) system [22]. The energetic model is based on a tight binding many-body potential for the metal-metal bonds and a surface energy potential approach fitted to ab initio calculations for the metal-oxide ones. The details of the energetic model description can be found in [22]. The parameters for the Ni-Ni interactions are given in [23] and the ones for the Ni-MgO (100) ones are listed in [24]. The Ni atomic relaxations are obtained by the quenched molecular dynamics procedure at 0 K, whereas the MgO (100) substrate is kept rigid. This approximation proved satisfactory for palladium clusters on MgO (100). In the case of Ni, the metal-oxide interaction is of a similar strength and the elastic properties of nickel differ only little from these of palladium. Based on the elasticity-derived arguments developed in [25] we estimate that nickel should accommodate the major part of the interface-induced distortion.

The coordinates of atoms in a Ni cluster supported on MgO obtained from molecular dynamic calculations were used for HRTEM simulations with the mutislice technique (the considered cluster contains about 4000 Ni atoms). For the cluster observed in profile view along a [100] direction (Fig. 5), the super-cell lattice parameters were a = 6.3150 nm and b = 4.7681 nm. For the cluster observed in profile view along a [110] direction (Fig. 7), the super-cell lattice parameters were a = 7.1570 nm and b = 4.9786 nm.

The calculations were performed with a resolution of 512×512 pixels. The defects in the simulated images (Fig. 6a) were evidenced in the image (Fig. 6b), four dislocations parallel to [100] are seen with a spacing of five



Fig. 4. (a), (b) Simulated images of the superimposition of $6 \times 6 \times 6$ unit cells of Ni layers on 5×5 unit cells of MgO with increasing thickness (respectively 42 nm and 63 nm).



Fig. 5. Equilibrium shape obtained by molecular dynamic calculation of a Ni cluster seen in profile view along [100].



Fig. 6a. Simulated HRTEM image by the multislice technique of the calculated Ni cluster (Fig. 5).



Fig. 6b. Filtered image in the Fourier space of the simulated HRTEM image of the cluster on Fig. 6a. The dislocations are indicated by arrows.



Fig. 7. Equilibrium shape of the Ni cluster on MgO (100) calculated by molecular dynamic simulation, seen in profile view along the [110] direction.



Fig. 8a. Simulated HRTEM image by the multislice technique of the calculated Ni cluster from Fig. 7.



Fig. 8b. Filtered image in the Fourier space of the simulated HRTEM image of the cluster on Fig. 8a, showing the dislocations present in the original image.

MgO layers. In the [110] direction, two defects in the calculated image (Fig. 8a) are better seen in the phase image (Fig. 8b).

In both cases, the distance between two dislocations is slightly lower than in the experimental images. Indeed, the HRTEM images correspond to the growth of seven Ni layers on six MgO layers, which represent a distance of 1.26 nm instead of 1.05 nm, between neighboring defects. This difference is due to the shortening of Ni-Ni distances inside the calculated cluster, where the experimental Ni-Ni distances preserve practically their bulk values. This shortening, induced by a large proportion of surface (under-coordinated) atoms, is somewhat overestimated in our model of metal-metal interaction. In the present case the effect may be additionally enhanced by the considerably different equilibrium shapes of the experimental and the calculated clusters, the latter being characterized by a larger aspect ratio. This difference can be hardly explained by deficiencies of the computational model. We remind that Pd clusters treated within the same framework showed a tendency to an underestimation of the aspect ratio [22]. Since in the present case we find an opposite effect, we tend to question the hypothesis of non-reactivity which is at the origin of the theoretical model, and suggest that nickel may oxidize to some extend at the experimental interface.



5. Discussion

Experimental images of the Ni/MgO interface in crosssection were obtained. They correspond to epitaxial relations: (001) Ni \parallel (001) MgO with [100] Ni \parallel [100] MgO. They show regular defects identified as dislocations, with a periodicity of 1.24 nm in the metal, in the three first layers from the interface with the oxide. This spacing between the defects corresponds to the superimposition of seven unit cells of Ni over six unit cells of MgO.

In the experimental image in top view of a Ni cluster on MgO, the moiré fringes are separated by 1 nm. Simulated images by the multislice technique of the superimposition of 6×6 unit cells of Ni on 5×5 unit cells of MgO, show moiré fringes with the same spacing, 1.08 nm.

The atomic structure of a Ni cluster on MgO was predicted by molecular dynamics calculations and the atoms coordinates were used to simulate the HRTEM image by the multislice technique. They clearly indicate defects with a spacing of five MgO unit cells and six Ni unit cells.

The misfit between bulk Ni (a = 0.352 nm) and MgO (a = 0.42 nm), is 17%. In order to accommodate Ni (001) on MgO (001), with Ni atoms located on oxygen ions, two coincidence meshes are possible. As observed in the experimental images, seven Ni atoms are superimposed on six oxygen ions in the [100] directions of MgO, which corresponds to a low misfit of 2.2%. The images obtained for the calculated cluster agree well with the experimental results, the slightly higher misfit (3.4%) being due to a stronger bond contraction within the calculated cluster. Whereas the experimental and calculated images in top view, normal to the Ni/MgO interface are in a good agreement, in profile view, the experimental images give a lower cluster's aspect ratio and reveal a better accommodation between the Ni and MgO lattices. In our opinion this may be due to a more complex structure of the experimental interface, with a possibility of partial oxidation of deposited nickel. This latter goes beyond the scope of our computational model.

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