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THE ANISOTROPY OF THE SURFACE ENERGY OF NICKEL MEASURED BY T.E.M. OF FIELD EMITTERS

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Résumé : La pointe de nickel d'un microscope à émission de champ est amenée à prendre une forme stationnaire en ultra-vide. Cette forme est ensuite examinée par transfert de la pointe dans un microscope électronique à transmission. On montre que la calotte au sommet d'une pointe bulbeuse coïncide avec la forme d'équilibre d'un cristal isolé de nickel. L'anisotropie de l'énergie de surface du nickel est déterminée en fonction de l'orientation cristalline.

Abstract : The stationary form of a clean nickel tip is produced in a field electron microscope (FEM) under ultra-high vacuum. The shape of the tip is then visualized in a transmission electron microscope (TEM). It is shown that the cap around the apex of a bulbous tip closely approximates the equilibrium shape of an isolated nickel crystal. The anisotropy of the surface energy (γ) of nickel is measured as a function of the crystallographic orientation.

I) INTRODUCTION :
The shape of field emission tips can be studied either by transmission electron microscopy [1] or by scanning electron microscopy [2]. The present paper is a transmission electron microscopy examination of clean nickel tips which has a two-fold aim:

a) Showing that the apex of a bulbous tip may closely coincide with the shape of an equilibrated single crystal, so that the anisotropy of the surface energy (γ) of the tip material can be determined by the inverse Wulff's construction.

b) Measuring the anisotropy of γ as a function of orientation along various crystallographic zones of a cubic f.c.c. crystal (Ni).

II) EXPERIMENTS :
The Nickel tips were prepared and cleaned in a FEM as already described [2] [3] [4]. After cleaning the tip a stationary form was installed by heating at 1300 K for a variable time (12 min to 2 h). The surface cleanliness was controlled by observing the FEM image and the change in tip radius was followed by measuring the emission current at a given voltage with the tip at room temperature. When no appreciable change occurred any more the tip was transferred to the specimen holder of a TEM equipped with two tilting facilities. In order to analyse a crystallographic zone the tip was tilted inside the TEM until two or more facets appeared as straight segments on the periphery of the tip profile. It was checked that the angles between the various faces were those required by crystallography within 1 degre. The <220> zone and sometimes the <200> zone could be visualized in this manner.

III) RESULTS AND DISCUSSION :

3-1) Due to the motion of grain boundaries during the heating process a rather severe selection had to be made among the tips to measure the anisotropy of γ correctly. Only three tips were deemed to be analysable which (i) had maintained a clean (111) oriented field emission pattern throughout the heating, (ii) showed a bulbous form upon examination in the TEM with a reasonably smooth and symmetrical shank in the vicinity of the apex, (iii) exhibited the symmetry properties that are described in the next sub-section.
3-2) Symmetry of the tip profiles:

The tip shape actually results from the competition between capillarity, which tends to blunt the tip by surface diffusion [5], and the driving force toward equilibrium due to the orientation dependence of the chemical potential of surface atoms, which tends to install the equilibrium shape. So the first step was to decide whether some parts of the profiles did coincide with the equilibrium profile of a nickel isolated crystal. This goal was achieved by considering whether the crystallographic symmetry axes of the cubic f.c.c. lattice were also symmetry elements of the profiles.

The crystallographic axes were constructed on the profiles by using purely geometrical considerations. Table 1 summarizes the method of construction. Figures 1a - 1b show the symmetry directions superimposed on the profiles of one tip. By definition point 0 is the intersection of [022] and [022] on the <200>-profile. Having measured the ratio h_{022}/h_{002} (with h the distances from 0 to the facets) point 0 was transferred to the <220>-profile as the particular point of [220] for which h_{220}/h_{002} had the same value. When the <200>-profile could not be visualized in the TEM (due to the limited tilt displacement available) 0 was located on the <220>-profile by using the h_{220}/h_{200} value that was measured for other tips.

![Fig. 1 TEM profiles of the same tip with the symmetry axes superimposed](image)

Table 1 also shows the results of the check of symmetry. To summarize, all the analysed profiles possess the symmetry which is required of an equilibrated cubic f.c.c. crystal within about 70° from the tip apex.*

* It is worth noting that the macroscopic axis of the tip does not necessarily lie in the profile plane (cf. fig 1 a) and may not coincide exactly with the [111] direction either (see fig. 1 b). This accounts for the lack of symmetry around [022] in fig 1a, for instance, since this region lies farther away than 70° from the tip apex. A more detailed analysis of this situation can be found in another paper [6].
Such a symmetry property is most remarkable. It shows that capillarity was not dominant at the apex of the particular tips we selected although the overall shape of the tip was a stationary form. If capillarity had been dominant the profiles would only have possessed symmetry with respect to the macroscopic tip axis. On the contrary we always found symmetry around the crystallographic axes of an equilibrated crystal even though these axes are away from the macroscopic axis of the tip. Therefore we assumed that the tip cap coincided with the true equilibrium shape of a nickel crystal within ca. 70° of the apex.

3-3) The γ-plot of clean nickel:
According to the conclusion just mentioned there exists a Wulff's point for the crystal around the apex. It has to be identified with point O. The γ-plot can then be determined by using the inverse Wulff's construction.

Figures 2 and 3 show the anisotropy of γ (normalised to γ_{111}) versus orientation for the <200> and the <220> zone respectively. Cusps are found at the directions where facets are observed on the profiles. The γ-plots of fig. 3 coincide within the uncertainty of the measurements. They are independent of the cleaning procedure and of the duration of the heating process. This shows the validity of transferring point O to the <220>-profile (section 3.2). The correctness of our procedure was further confirmed by another test which is described in a more detailed paper [6].

Only a few experimental measurements of the anisotropy of γ for nickel are available. Mykura [7] found a slightly greater anisotropy but ascribed it to some pollution of the crystal surface. Maiya and Blakely measured absolute values of γ: γ_{220} = 1911 ± 190 erg. cm^{-2} and γ_{200} = 1821 ± 182 erg. cm^{-2}. This yields γ_{200}/γ_{220} = 1.05, a greater value than our present result, but the uncertainty involved in absolute measurements prevents a meaningful comparison to be made. A model calculation after the theoretical data of Drechsler and Nicholas [1] is shown by the solid line in fig. 3. Considering the imperfection of broken-bonds models the overall agreement is satisfactory.

IV) CONCLUSION:
1) The cap at the apex of a bulbous FEM tip can be used to determine the γ-plot of the tip material.
2) The orientation dependence of the surface energy of clean nickel has been measured over the two essential crystal zones <200> and <220>.

Our experiments confirm that the γ-plot of high melting point metals can be measured by a combined FEM-TEM method.

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Fig. 3. The y-plots of three nickel tips for the $<2\overline{2}0>$ zone. (● ● ●) experimental points. Solid line: theoretical values at 1200 K.

### Table 1

Construction of the major crystallographic directions of the profiles and measured symmetry relationships.

<table>
<thead>
<tr>
<th>Direction [hkl]</th>
<th>[022]</th>
<th>[027]</th>
<th>[020]</th>
<th>[002]</th>
<th>[220]</th>
<th>[002]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method of construction</td>
<td>Bisector of the angle between (020) and (002) such that $b_{022} = b_{022}$</td>
<td>Normal to (022) 0 to (020)</td>
<td>Normal from 0 to (020) 0 to (002)</td>
<td></td>
<td>Bisector of the angle between (111) and (111)</td>
<td></td>
</tr>
<tr>
<td>Is [hkl] the mediator of (hkl)?</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Is [hkl] a symmetry axis of the profile?</td>
<td>Yes</td>
<td>No (a)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(a) $b_{022}$, $b_{022}$ are the central distances to (022) and (022) respectively 
(b) $b$ is the intersection of [022] and [022] for this profile 
(c) $b$ is constructed as explained in the text 
(d) Provided the center of (002) is within ca. 70° of the apex (see text) 
(e) The regions to the left of (022) (cf. fig. 3a) are farther away than 70° from the apex (see text)

### References