THE FACES ON MICRO-CRYSTALS (FIELD EMITTERS, CATALYST PARTICLES)

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Résumé - Le diamètre d'une face d'un micro-cristal est décrit comme fonction du rayon de courbure de la surface. Une face hkl apparaît seulement si le rayon est supérieur à une valeur limite. Une étude en microscopie ionique confirme ces prédictions. Les faces d'une particule catalytique (Pt) sont déterminées par analyse de l'image électronique du cristal.

Abstract - The diameter of a face on a micro-crystal is described as a function of the surface curvature radius. A face hkl appears only above a special limit radius. A field ion microscope study confirms such predictions. The faces on a Pt catalyst particle are determined by analysis of an electron micrograph of the crystal.

INTRODUCTION

The basic problem studied in this paper is: what hkl faces are present on a crystal? For macroscopic polyhedral crystals this problem has been solved in the 19th century. It is known that the crystal surface is often not a polyhedron, but composed of plane faces and curved regions (see /1/). This has been found on field emitter crystals as well as on metal crystals grown on a support. A curved region is composed of many extreme small hkl faces, which is a consequence of the atomic crystal structure. So questions arise as: what hkl faces exist on the curved regions? What are the diameters of such faces? How does a diameter change with the surface curvature or the crystal diameter? A special answer to the last question is given by the theory of equilibrium shapes (Gibbs, Wulff), namely: Relative diameters should be independent of the crystal size. This is true for macroscopic crystals, where a lattice plane distance is practically infinitely small. However, as we will show here for face and bodycentered cubic crystals (fcc, bcc) on micro-crystals the diameter of a face must change with the crystal size. Furtheron we compare the result with field ion micrographs and finally use it for a first attempt to determine the faces on a metal particle of a catalyst (see also /2/).

THE DIAMETER OF A FACE AS A FUNCTION OF THE SURFACE CURVATURE

In the following it is for simplicity assumed that the cross section of a curved crystal region has a constant curvature radius r at least along a certain region. This assumption is roughly confirmed by micro-crystal curvature measurements on crystal profile images obtained by transmission or scanning electron microscopes (TEM,SEM).
Using geometry and statistics it can be shown that the mean diameter $(2g)$ of an hkl face of a cubic crystal (fcc, bcc) is:

$$2g = \frac{a}{3} \left[ 3a \left( h^2 + k^2 + l^2 \right)^{-1/2} \right]^{1/2}$$

$a$ = lattice parameter, hkl are the crystallographic face indices.

A face can exist only if its diameter is greater than the distance $s$ between neighbouring atom chains of the outer lattice plane. Consequently a face hkl can exist only above a limit curvature radius $r_m$. The value of $r_m$ is:

$$r_m \approx 0.2 \frac{s^2}{d} - \frac{d}{3} \quad \text{and} \quad d = a/\left( h^2 + k^2 + l^2 \right)^{1/2}$$

d = lattice plane distance of hkl. Quantitative data of these equations are presented in diagrams and tables for more than 40 types of fcc and bcc faces.

Some general results are:

1. The surface of extreme small crystals ($< \approx 20$ Å) is composed nearly only of closest packed faces.
2. When a crystal is growing from $\approx 20$ Å to $\approx 200$ Å medium index faces (for example (024)) begin to appear (the curvature radius is assumed to be in the order of 0.2 of the crystal diameter).
3. High index faces (for example (446)) appear only above $\approx 200$ Å crystal size.
4. Very high index faces or faces with greater step distances can appear only on relatively great crystals, for example faces of $\approx 20$ Å step distance on crystals greater than $\approx 1$ μm and those of 40 Å step distance on crystals greater than $\approx 10$ μm.
5. Point (4) has a consequence for the equilibrium shapes of clean metal crystals. Experimental equilibrium shape studies are made on crystals up to $\approx 10 \mu$m size including field emitter crystal studies (see /1/). Such shapes can not exactly be those calculated using surface free energy anisotropies. The real equilibrium shapes must be modified for a very small crystal. For example the angle between a close packed face and its nearest vicinal face can not have a constant value (its value is even controversial /3/). Rather this angle must increase with decreasing crystal size in a manner which is calculable using data of equ. 1 and 2.
6. The diameter of a real face is only one of a calculable diameter distribution. So a comparison between calculated and measured data requires statistical measurements of the diameter of one face leading to a diameter distribution and then the mean value of this distribution has to be compared with the calculated mean diameter.

CONTROL OF THE APPEARANCE AND SIZE OF FACES BY FIELD ION MICROSCOPY

The calculated appearances and the diameters of the faces can be controled by field ion microscopy (FIM). For such a control it has to be considered that the curvature radius along a field evaporated tip surface varies in a special manner, which can be determined by FIM micrograph analysis /4/. The control has been made by analysing micrographs of tungsten tips of different mean radii (30 Å, 60 Å, 270 Å and 600 Å) taken by M. ADDIFFREN and J. BARDON in our laboratory in the course of a former study. The result of many controls is: All face appearances (limit radii) and all face diameters determined from the micrographs are in reasonable agreement with the corresponding data calculated using equation 1 and 2.

FACE ANALYSIS BY ELECTRON MICROSCOPY (FIELD EMITTER CRYSTALS, CATALYST PARTICLES)

The faces of heated crystals formed by surface self-diffusion can not be analysed
using the FIM. In such cases the analysis can be made by measuring surface curvature 
radii along special zones by electron microscopy (TEM, SEM) /1//4/ and the use of 
equ. 1 and 2. Recently we have realized a first attempt to analyse faces on much 
smaller crystals, i.e. on supported platinum particles of a catalyst used in che-
   mical industry /2/. The particles were visualized by TEM (micrographs taken by 
R.M. RICKARD of our laboratory). Then, curvature radius measurements in combination 
with equ. 1 and 2 lead to the result that on a 20 Å particle (zone [220]) only 
close packed faces exist ((111) and (002)). However, on a 70 Å particle at least 
(113) and (331) are analysed as additional faces. As the additional faces have 
certainly a different catalytic activity, it can be supposed that the experimentally 
known activity change as a function of the particle size is at least in some cases 
a consequence of the described appearence of additional faces. Nevertheless more 
studies in this direction are required to verify this hypothesis.

DISCUSSION

By using the face analysis described here one should be aware that the ideal atomic 
surface structure of a face is modifiable by adsorbates, relaxation, reconstruction 
and thermal roughening and the information on such phenomena is usually very poor. 
But the ignorance of such structure details does not change the fact that the deter-
mination of the hkl values and the size of a face is of basic importance.

OUTLOOK

The results briefly described here may stimulate :

(1) to improve the determination of the hkl values of high index faces in field 
    ion microscopy,

(2) to verify experimentally the predicted change of the equilibrium shape for 
    very small crystals,

(3) to study systematically the appearence of faces on catalyst particles in view 
    of future attempts to correlate changes of face appearences (due to particle size 
    changes) with changes in the catalytic activity.

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