Method for determining the surface energy of nitrides, carbides and borides

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Abstract. The article reviews the existing methods for determining the surface energy of solids. Each of the methods described is practically limited to either temperature or values that are experimentally determined with low accuracy. A method is proposed for determining the surface energy of a solid on the basis of the dimensional dependence of its physical properties (magnetic permeability, luminescence intensity, thermal conductivity, etc.). The surface energy of some nitrides, borides and carbides is determined. Its magnitude is much larger than the surface energy of pure metals. The critical radius of nitrides, borides and carbides is calculated, from which the direct Hall-Petch effect is reversed.

1. Introduction

Methods for determining the surface energy of solids began to be developed in the 20s of the last century [1, 2]. In the sixties of the last century, some results of research were presented [3, 4]. The following methods for determining the surface energy of solids were proposed [3, 4]:
1. The method of "zero creep".
2. Method of destruction (splitting) of crystals.
3. The "neutral drop" method.
4. Method of dissolving the powder
5. The method of stages of growth and evaporation.
6. The method of a conical sample.
7. Method of "healing scratch".

The zero creep method is fundamentally in the following points. Due to the surface tension forces at high temperature, the length of the thin metallic thread increases in the direction of the total surface energy. After applying an external force (P), the metallic thread begins to elongate under the influence of a viscous flow. At a certain value \( P = P^1 \), the surface tension forces are compensated and the creep rate becomes zero. The value of the force \( P^1 \) characterizes the magnitude of the surface tension. This method is applicable to pure metals at a temperature almost equal to the melting point. For most metals (and there are 98 of them in the periodic table of elements), this method determines the value of the surface energy. It is believed that the zero creep method is the most accurate. For other materials, this method is not used, due to the complexity of its practical implementation.

The most reliable version of the method of determination, based on cleavage of the crystal, was proposed in 1930 Obreimov [2]. The idea of this work is as follows. From the crystal along the cleavage plane, plastic is split off, which under the influence of the moment of forces acting against the forces of surface tension, partially bends. This plate can be used as a dynamometer measuring the splitting force. The method was applied in [3] (Gilman J.) for various crystals at a temperature of liquid nitrogen, when the heat arising from the splitting of the crystals can be neglected. The method is suitable for crystals having a cleavage plane.
The value of $\sigma_s$ can be determined from the data on the equilibrium form of the liquid droplet of another substance, which is located on the surface of the solid under study. The measurement scheme is clear from Fig. 1.

![Diagram of the "neutral drop"](image)

**Figure 1. Diagram of the "neutral drop"**

In the method for dissolving the powder, the value is found from the calorimetric determination of the dissolution heat difference of the dispersed powder and a massive crystal of the same mass ($\sigma_s = q_r - q_0/S$). The source of the significant error in the method described is the inaccuracy in the determination of the total surface of the powders. The generally accepted assumptions that the shape of the powder are spherical and all the powders are the same can lead to large errors.

To determine the amount of surface energy in the method of growth and evaporation stages, one uses the fact that on the growth surface there are often observed retarded "resting" steps whose curvature is such that the equilibrium vapor pressure near the step surface coincides with the vapor pressure in the space surrounding the crystal. The accuracy of the method is small.

Directly in the method of a conical sample, not the surface energy but the quantity (interfacial surface tension at the liquid-solid interface) is determined at the melting temperature [4]. The method is rarely used.

It is known that in the case of high-temperature annealing of a crystal under equilibrium conditions, on the surface of which a scratch is applied, the latter is smoothed out. For metals, the kinetics of smoothing is determined by the mechanism of surface diffusion. This is the basis of the method of "healing scratch" [4].

As follows from the review [1-4] of experimental methods for determining the surface energy of solids, each of the methods described is practically limited to either temperature or values that are experimentally determined with low accuracy.

Currently, the most widespread are various modifications of the "neutral drop" method. The basis of this method is the Young equation [5], which leads to the concept of the contact angle $\theta$ (Figure 1). To describe the contact angle on a real surface, two different approaches are used – the Wenzel model and the Cassie-Baxter model. The difference between these two models lies in the fact that Wenzel considers a rough surface with a chemical mosaic [6]. The Cassie-Baxter model uses the notion of a flat surface with chemical heterogeneity [7].

These models have been widely used to date. However, today they have come under serious criticism [8]. More complex contact angle models have been developed, for example, in [9-13].

In [13], the Young equation, the Wenzel equation, and the Cassie – Baxter equations were obtained using classical thermodynamics. In this case, it was possible to predict a change in the contact angle, which consisted in the fact that it is determined by a small area near the outer contact line, as opposed to the inner surface. In this case, the contact angle does not depend on external factors and on the surface tension. It was also shown in [13] that the Cassie – Baxter equation leads to erroneous results, despite its wide use, especially for the superhydrophobic surface. In the same paper, it is emphasized that the thermodynamic approach is preferred because it is free from constraints and its size is not affected by the size of the drop and the curvature of the surface.
The real surface is complicated by adsorption processes, the complexity of the morphological relief and a number of other factors. All this together is necessary for a deeper understanding of the nature of the contact angle.

2. Statement of a problem
Of covalent carbides, nitrides and borides, diamond-like compounds are of particular interest. They are formed by elements with close electronegativities and a tendency to sp3-hybridization. Usually these are binary compounds of the type AIIIBV and AIVBIV. The type of hybridization determines their crystal structure, so they are called tetrahedral phases. Ionicity of communication in them is insignificant. These compounds are very refractory and superhard. Typical representatives of diamond-like compounds are borides and carbides of nitrogen and silicon. Recently, the possibility of their use as high-entropic coatings has been considered [14]. It is very important for them to determine the surface energy, which determines the surface properties of these compounds.

3. Theory
The foundations of the thermodynamics of curvilinear interfaces were laid by J. Gibbs [15]. Then R. Tolman and his followers reduced this problem to the account of the dimensional dependence of the surface tension. In 1949, R. Tolman derived the equation for the surface tension \( \sigma \) [16]

\[
\frac{\sigma}{\sigma_\infty} = (1 + 2\delta / R_s)^{-1}
\]

Here \( \sigma_\infty \) is the surface tension for a plane surface; \( R_s \) is the radius of the tension surface; \( \delta > 0 \) is the distance between an equimolecular separating surface and a tension surface for a plane boundary. The order of magnitude of the parameter \( \delta \), called the Tolman length or the Tolman constant, should be comparable to the effective molecular diameter \( a \). For \( R_s \gg \delta \) Tolman's formula can be rewritten in the form:

\[
\frac{\sigma}{\sigma_\infty} = 1 - 2\delta / R
\]

Subsequent studies did not change the content and form of the equation (2).

On the basis of quantum statistical thermodynamics we obtained the response function of the system \( W \) to the external action in the form [17]:

\[
\frac{W}{W_\infty} = 1 - d / R
\]

The parameter \( d \) is related to the surface tension \( \sigma \) by the formula [17]:

\[
d = \frac{2\sigma \nu}{RT}
\]

Here \( \sigma \) is the surface tension of a massive sample; \( \nu \) is the volume of one mole; \( R \) is the gas constant; \( T \)-temperature.

Equations (3) and (4) were used by us to develop a method for determining the surface tension of solids [18]. The method was used to determine the surface tension of dielectric crystals KCl, with an admixture of thallium ions as a luminescent probe (\( W = 1 \)). The intensity of X-ray luminescence I was determined by the standard photoelectric method. The grain size of the dielectric was determined using a metallographic microscope. The results are shown in Fig. 2. In the coordinates \( I \sim 1/r \), the experimental curve is rectified in accordance with (3), giving a value of \( d = 0.02 \mu \text{m} \). For KCl \( \nu = 74.6 \text{ cm}^3/\text{mol} \) and from (4) for surface tension, we obtained: \( \sigma = 0.730 \text{ J/m}^2 \).
Figure 2. Dependence of the intensity of X-ray luminescence KCl on the size of the phosphor grain.

Note that as a function of the W response in equation (3), most physical properties that depend on the particle size or the film thickness (magnetic susceptibility, dielectric constant, thermal conductivity, etc.) can be used and determine the surface tension of a rigid body. As an example, Figure 3 shows the dimensional dependence of the magnetic susceptibility of magnetite.

Figure 3. Dependence of the relative magnetic susceptibility on the grain diameter of magnetite Fe₃O₄.

4. Results of the experiments and discussion

In the present work, the method of luminescing probes was mainly used. The results of the materials studied are presented in Table 1. Here the mean values of the surface tension are disregarded, without taking into account the anisotropy of the various crystalline faces.

| Nitrid | σ, J/m² | Borid | σ, J/m² | Carbid | σ, J/m² |
|--------|---------|-------|---------|--------|---------|
| TiN    | 2.062   | TiB₂  | 2.258   | TiC    | 2.203   |
| ZrN    | 2.069   | ZrB₂  | 2.258   | ZrC    | 2.471   |
| HfN    | 2.331   | HfB₂  | 2.336   | HfC    | 2.721   |
| NbN    | 1.624   | NbB₂  | 2.125   | NbC    | 2.436   |
| TaN    | 2.352   | TaB₂  | 2.125   | TaC    | 2.716   |
Studies of the mechanical properties of nanoparticles, nanomaterials and nanostructured coatings have shown that both the hardness of metals and the tensile strength (Pd, Cu, Ag, Ni, etc.) are greater than those in bulk samples. The decrease in the average grain size is accompanied by an increase in strength and hardness to a certain limit. This is observed for almost any material. Such behavior of the yield stress $\sigma_T$ is described by the Hall – Petch equation [19, 20], according to which the yield strength is inversely proportional to the grain size $d$:

$$\sigma_T = \sigma_M + kd^{-1/2},$$  \hspace{1cm} (5)

where $\sigma_M$ is the ultimate strength of a single crystal, $k$ is a certain dimensional coefficient. Equation (5) is valid for many of the studied nanoparticles and nanomaterials, but most often up to a certain grain size. At lower grain values, inverse dimensional effects are often observed, at which strength and hardness decrease. Table 2 shows the $d$ values calculated by the formula (4).

### Table 2. Parameter $d$ of nitrides, borides and carbides

| Nitrid  | $d$, nm | Borid   | $d$, nm | Carbid  | $d$, nm |
|---------|---------|---------|---------|---------|---------|
| TiN     | 10.2    | TiB$_2$ | 12.6    | TiC     | 10.6    |
| ZrN     | 17.4    | ZrB$_2$ | 20.4    | ZrC     | 20.4    |
| HfN     | 35.9    | HfB$_2$ | 37.4    | HfC     | 41.9    |
| NbN     | 13.9    | NbB$_2$ | 17.6    | NbC     | 20.5    |
| TaN     | 36.7    | TaB$_2$ | 34.4    | TaC     | 41.9    |

The physical reasons for the violation of the Hall-Petch law (5) remain the subject of numerous discussions, despite the solid period of these studies (over 50 years) [21-26]. In [27] for the yield point we obtained the equation:

$$\sigma_T = \sigma_M + Cd^{-1/2}.$$  \hspace{1cm} (6)

Equations (5) and (6) formally coincide with each other, but the proportionality coefficients differ significantly. The yield strength of nanoparticles in accordance with equation (6) is determined, in addition, by the magnitude of the surface tension $\sigma$.

For small values of $d$ in [28], Rusanov A.I. got an asymptotic linear relationship:

$$\sigma = Kd.$$  \hspace{1cm} (7)

In formula (7), the proportionality coefficient $K$ is constant. This formula is obtained by general thermodynamic consideration and is valid in the case of small objects of any nature. In this case, equation (6) takes the form:

$$\sigma_T = \sigma_M + Ckd^{1/2}.$$  \hspace{1cm} (8)

Equation (8) is the inverse Hall-Petch effect. The Hall-Petch law begins to be violated when the dimensional dependence of surface tension ($R < d$) begins to manifest itself, as follows from equation (6).

It can be seen from Table 2 that the strength is replaced by plasticity at rather large $d$ values (for borides of hafnium and tantalum, $d = 41.9$ nm). In Table 3, for comparison, the values of $d$ for pure metals are given.

Table 3 shows that the parameter $d$ of pure metals does not exceed 10 nm. For example, for tungsten, the critical radius is 8.4 nm, i.e. Within the limits of experimental error, it coincides with the experimental value.

Comparison of Tables 2 and 3 shows that the parameter $d$ for pure metals is significantly less than for chemical compounds (nitrides, borides, carbides).

### Table 3. Parameter $d$ of pure metals (M)

| М   | $d$, nm | M   | $d$, nm | M   | $d$, nm | M   | $d$, nm | M   | $d$, nm | M   | $d$, nm |
|-----|---------|-----|---------|-----|---------|-----|---------|-----|---------|-----|---------|
Li 1.4 Sr 8.3 Sn 2.0 Cd 1.9 Fe 3.1 Gd 7.6
Na 2.1 Ba 8.9 Pb 2.6 Hg 0.8 Co 2.8 Tb 7.5
K 3.7 Al 2.2 Se 1.9 Cr 3.8 Ni 2.7 Dy 7.6
Rb 4.2 Ga 0.9 Te 3.5 Mo 6.5 Ce 5.4 Ho 7.8
Cs 5.2 In 1.6 Cu 2.3 W 8.4 Pr 6.0 Er 7.8
Be 1.8 Tl 2.4 Ag 3.1 Mn 2.8 Nd 6.4 Tm 7.4
Mg 3.1 Si 4.9 Au 3.3 Tc 5.1 Sm 6.3 Yb 6.5
Ca 7.0 Ge 4.0 Zn 1.5 Re 7.1 Eu 8.3 Lu 8.2

5. Conclusion
The proposed method for determining the surface energy of a solid body with respect to the dimensional dependence of its physical property allows one to make a comparison with several methods. The implementation of each method does not cause any difficulties. This is illustrated by the calculation of the surface energy of nitrides, borides and carbides.

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