



Model of coordination melting of crystals and anisotropy of physical and chemical properties of the surface



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ABSTRACT

Based on the evaluation of the properties of crystals, such as surface energy and its anisotropy, the surface melting temperature, the anisotropy of the work function of the electron, and the anisotropy of adsorption, were shown the advantages of the model of coordination melting (MCM) in calculating the surface properties of crystals. The model of coordination melting makes it possible to calculate with an acceptable accuracy the specific surface energy of the crystals, the anisotropy of the surface energy, the habit of the natural crystals, the temperature of surface melting of the crystal, the anisotropy of the electron work function and the anisotropy of the adhesive properties of single-crystal surfaces.

The advantage of our model is the simplicity of evaluating the surface properties of the crystal based on the data given in the reference literature. In this case, there is no need for a complex mathematical tool, which is used in calculations using quantum chemistry or modeling by molecular dynamics.

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1. Introduction

Melting of solids is a well-studied example of the phase transition of the first kind. However at present there has not been created a unified melting process theory describing the mechanism and driving forces of the macro- and micro-level phenomena that occur in this transformation phase. Ubbelohde suggested that the crystal melting starts on its surface because of the energy excess stored as a surface energy. Herewith the surface melting temperature of crystallographically different surfaces must differ from each other due to the differences in the specific surface energy values of these surfaces [1]. The Ubbelohde model assumes a difference in the melting temperatures of crystallographically different surfaces, which should lead to a change in the shape of the crystals at a temperature close to the melting point. However, this phenomenon was not found experimentally. Based on Lindemann's criterion Zangwill came to the conclusion on the layer-by-layer melting of a crystal because of the increased amplitude of the surface atoms vibrations compared to the crystal bulk atoms [2]. However, the Zangwill model considered only a monatomic surface layer of atoms, without considering the differences in the amplitude of the vibrations of surface atoms on crystallographically different surfaces of the crystal. At present numerous experiments data and model calculations have confirmed the irregularity of crystal melting start and proved the existence of the surface melting of crystals [3–6].

In this study we consider the model of coordination melting of crystal (MCM). According to this model, the surface layer of a crystal begins to melt at a temperature lower than the bulk melting temperature for this substance due to the presence of surface energy [7,8]. It is assumed that the minimum thickness of the melt surface layer is equal to the thickness of the first coordination sphere of atoms (molecules) in the given crystallographic direction.

This model is based on the energy criterion of crystal melting, according to which the melting of crystals begins at the moment of accumulation of internal energy equal to the enthalpy of the crystal at the melting point, regardless of the form of energy storage [9].

2. Material and methods

It is known that the enthalpy change when the crystal is heated to the melting point is:

$$\Delta H = \int_0^{T_m} C_p \cdot dT \quad (1)$$

where C_p is thermal capacity of the crystal, T_m - melting temperature, H - enthalpy. We take the value of the enthalpy at the melting temperature as an "energy criteria" of the crystal transition into an amorphous phase independently of the way it gets that. In case this is a cracking process, then, considering that the mechanic energy is realized in increasing the crystal total surface energy $\Sigma\sigma_{hkl}$ during its dispersion, we can suppose the moment of amorphisation comes when $\Sigma\sigma_{hkl}$ becomes

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equal ΔH when the crystal is at 0 K, or

$$\Delta H^* = \int_T^{T_m} C_p \cdot dT \quad \text{if } T < T_m \quad (2)$$

Having done such a supposition we can evaluate the critical size of the crystal that is special for its transition into the amorphous state. As a first approximation we shall consider cracking of the crystal into separate cubic crystals. The full surface energy of one of these crystals is

$$E = L^2 \cdot \sum_{i=1}^6 \sigma_i \quad (3)$$

where L is the crystal linear size, and σ_i - the specific surface energy of the surfaces i . For cubic symmetric crystals this expression is taken as:

$$E = 6L^2 \cdot \sigma_{hkl} \quad (4)$$

where σ_{hkl} is the specific surface energy of the surfaces (hkl) of the given crystal.

Using the main supposition we get the expression characterizing the transition of the crystalline phase into the amorphous one at an arbitrary temperature [9]:

$$k \cdot \int_T^{T_m} C_p \cdot dT = L^2 \cdot \sum_{i=1}^6 \sigma_i \quad (5)$$

where k — molar coefficient that is equal to the number of grains in the mole of the substance ($k = L^3 / V$, $V = M / \rho$ – the mole volume, M – atomic weight, ρ – density of the crystal). From Eq. (5) the minimum linear size of the crystal cubic grain is easily evaluated at $T < T_m$, further decreasing of it takes it to the amorphous phase:

$$L = V \cdot \left(\sum_{i=1}^6 \sigma_i \right) / \int_T^{T_m} C_p \cdot dT \quad (6)$$

Suppose that the melting begins with the transition into the surface layer melt, with thickness - L_{hkl} is equal to the thickness of the first coordination sphere of atom in this crystallographic direction [7]. For the crystals with lattices of the BCC, FCC and HCP types this thickness is equal to the double interlayer distance in this crystallographic direction [7,8]:

$$\text{Pm}\bar{3}\text{m}, Z = 1 : L_{100} = 2a; L_{110} = a\sqrt{2}; L_{111} = 2a/\sqrt{3} \quad (7)$$

$$\text{Im}\bar{3}\text{m}, Z = 2 : L_{100} = a; L_{110} = a\sqrt{2}; L_{111} = a/\sqrt{3} \quad (8)$$

$$\text{Fm}\bar{3}\text{m}, Z = 4 : L_{100} = a; L_{110} = a/\sqrt{2}; L_{111} = 2a/\sqrt{3} \quad (9)$$

$$\text{Fd}\bar{3}\text{m}, Z = 8 : L_{100} = 0,5a; L_{110} = a/\sqrt{2}; L_{111} = 2a/\sqrt{3} \quad (10)$$

3. Theory/Calculation

Consider the value of the internal energy of one mole of the surface layer with the thickness of the first coordinate sphere in the direction [hkl] by the moment of the crystal melting. It can be evaluated according to the formula:

$$U_1 = \left(\frac{S \cdot L_{hkl} \cdot \rho}{M} \right) \cdot \int_0^{T_m} C_p dT + \sigma_{hkl} \cdot S + U_0 \quad (11)$$

where $\left(\frac{S \cdot L_{hkl} \cdot \rho}{M} \right)$ – mole coefficient that is equal to the layer volume divided by one mole volume, T_m – the crystal melting temperature, C_p – its thermal capacity at 298 K, U_0 – internal energy at 0 K, ρ – its density, M – atomic weight, S – surface area (hkl), L_{hkl} – the thickness of the first coordinate sphere towards [hkl], and σ_{hkl} – the value of the specific surface energy (hkl).

To simplify the calculations we shall ignore the temperature dependences of ρ , L_{hkl} and C_p , considering them as constants.

Let us consider the same layer separated from the crystal at 0 K. Such layer has a long-range ordering only in two independent directions inside the layer, and in the direction which is perpendicular to the layer the atom arrangement ordering is limited with the thickness of the first coordination sphere. Physically this layer is not already in the crystalline state, it is in the state of transition from crystal into liquid. The internal energy saved in this layer is:

$$U_2 = 2\sigma_{hkl} \cdot S + U_0 \quad (12)$$

In both cases (11) and (12) the energy values show the start of transition of the same crystalline substance amount into liquid state. Equating them to each other we get the formula for the crystalline substance surface energy calculation according to the MCM:

$$\left(\frac{S \cdot L_{hkl} \cdot \rho}{M} \right) \cdot \int_0^{T_m} C_p dT + \sigma_{hkl} \cdot S + U_0 = 2\sigma_{hkl} \cdot S + U_0 \quad (13)$$

or

$$\sigma_{hkl} = \left(\frac{L_{hkl}}{M} \cdot \rho \right) \cdot \int_0^{T_m} C_p dT \quad (14)$$

The obtained formula makes it possible to calculate the anisotropy of the surface energy on crystallographically different surfaces of the crystal without complicated, labor-intensive calculations with limited capacity applying the quantum chemistry and molecular dynamics simulation [7]. Since L_{hkl} is constant for a given spatial symmetry group, it follows the formula (14), that the anisotropy of the surface energy is constant for all metals that crystallize in the same structural type.

4. Results

4.1. Calculation of values of specific surface energies of metals

We calculate the surface energy of a number of metals from the model of coordination melting of crystals (formula 14).

Table 1 gives the specific surface energy values calculated with the MCM, in comparison with the other theoretical results.

As we can see from Table 1, the anisotropy of the surface energy calculated with the MCM is constant for a given symmetry of the crystal structure of metals, in contrast to the other calculations available in the literature, which confirms its plausibility. An exception is the calculation of the anisotropy of the surface energy from Caglioti et al. [12], which generally confirms our calculations.

Fig. 1 shows the maximum values of the surface energies of a number of metals, calculated with the MCM and from other literature data.

It should be noted that the values of the specific surface energy obtained by different authors often differ from each other for more than 20%. Therefore, the values of the specific surface energy of different faces should be judged by its anisotropy.

Table 2 shows the anisotropy values of the specific surface energy calculated with the MCM compared to the experimental and other theoretical values. It can be seen from Table 2 that the anisotropy calculated with the MCM and obtained experimentally coincides completely.

The correctness of our calculations of the anisotropy of surface energies is confirmed by the calculated data of Caglioti et al. [12, 13] and the experimental values of the anisotropy of the surface energy from Nelson and co-workers [14,15] (see Tables 1 and 2). As can be seen from the Table 2, the anisotropy calculated by us coincides with the anisotropy obtained experimentally and calculated from Caglioti et al. [12,13] but the anisotropy calculated from Wang and Wang [11] contradicts the experimental value [14].

4.2. The connection of surface energy with the habit of crystals

It has turned out that faceting of natural crystals mostly correlated with the calculated specific surface energy values, and the maximum specific surface energy values comply with the most developed faces [16]. In Table 3 it is shown that the anisotropy of the surface energy

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