THERMODYNAMICS OF SINGLE- AND POLYCRYSTALS DEFECTIVE STRUCTURE

V. FEDOSEEV

Melnikova-Pecherscogo, 8-177,
603057, Nizhny Novgorod, Russia

ABSTRACT

The work continues investigations on successful usage of chemical thermodynamics for crystal lattice defects such as dislocations, pores, dislocation loops, etc. At present neither physical chemistry nor solid state physics provide such theoretical models which can adequately describe the dislocation density in annealing crystals under the different thermodynamic conditions. The theoretical estimation of macro defect density proved to be effective while discussing crystal physical properties such as strength, plasticity, frangibility, surface melding. The performed calculations allow to find out some interesting regularities associated with pressure and temperature effects on defective structure of crystals as well as to set up a relation between a crystal size and macro defect density.

KEYWORD

The equilibrium density of dislocations. The effect of pressure, temperature, crystal size on defective structure. The surface melting, phase transitions on crystal surface.

GROUNDS.

Physical and chemical properties of crystals are of a great extent determined by composition and density of defects on material surface and in its' volume. The modern theory allows to describe the behavior of point defects in crystal lattice: vacancies, interstitial atoms, admixture atoms. However, large defects of crystal lattice such as dislocation loops, pores, edge dislocations, grain boundaries and etc. are offen more essential. Neither physical chemistry nor solid state physics are capable nowadays to determine behavior, number and composition of these macro defects.

The author of the work managed to propose a model

providing an adequate description of macro defect density for some particular cases: ensembles of circular dislocation loops, straight edge dislocations (Fedoseev, 1989-1991), spherical and faceted pores and gas bubbles at different temperatures, hydrostatic pressures and crystal size. The model eliminates discrepancy between experimental observations showing, that it is impossible to obtain single crystals of metals with dislocation density about 10^5 - 10^{11} om^2 and theory of dislocation stating that in metal in thermodynamic equilibrium dislocations should not exist at all.

The idea, that dislocations can not exist in crystal in thermodynamic equilibrium is based on classical works of Cottrell, Hirt and Lothe, Girifalko, Fridel and ets'. This statement is a result of quantitative estimation of dislocations equilibrium density According to this estimation the number of dislocation loops with radius 30 Å at room temperature should be equal to $\approx 10^{-178}$ per om^3, or one equilibrium loop per single crystal, with volume exceeding visible part of the Universe!!!

For example, Lothe and Hirth (1972) do this in the following way. Let the free energy of formation of circular dislocation loop be equal to the difference between the internal loop energy and free energy of lattice vacancy (the loop can be formed by collapse of this lattice vacancy). Total neglect of dislocation entropy in this case is not correct, because - configurational and orientation entropies of the loop and the entropy connected with the existence of a great number of partitions vacancy on several defects appears to be very big. Besides, the value $kT*ln(C(0.5*T_{melding})/C(T_{melding}))$, where k - Boltzmann constant, T - temperature, C(T) - density of vacances, is not the chemical potential of vacancy under no condition, that is why the free energy of vacancy is calculated incorrectly.

The incorrect use of notions and principles of statistical thermodynamics makes some authors adjust turn the corresponding quantitative estimation to the statement about "nonequilibrium" of dislocation. The critical analysis of these works lies beyond the scope of this report.

THERMODYNAMIC MODEL.

The proposed thermodynamic description of defective crystal structure is based on equilibrium chemical thermodynamics using methods of theory of dislocations (Fridel, Lothe and Hirth). The basic concept of this approach involves a sequential description of macro defects such as dislocations, pores and etc. in terms of chemical thermodynamics, equilibrium state of a crystal is determined by minimization of the Gibbs free-energy system having variable quantity of components (pores, dislocation loops, etc.), number of which changes due to evaporation and condensation of vacancies, coalescence and dissociation of large pores and dislocations.

The results in agreement with the experiments can be obtained, if one uses the model suggested by the author. The basic statements of the model which describe the thermodynamic equilibrium of defect structure of crystal are:

\# In crystal with the sizes $L*L*L$, which contains $N \sim L^3$ atoms the number of atoms does not depend on the density of dislocation and does not change for any reconstruction of dislocation structure.

\# Each dislocation (pore and other defects) has individual thermodynamic characteristics:
- the internal energy of formation
- the enthalpy of formation
- the entropy of formation
- the volume
- the stoichiometrical number of the defect. (It is the number of atoms to be moved in ideal crystal lattice to form the corresponding defect)

\# The internal energy and enthalpy of crystal defect structure are additive:
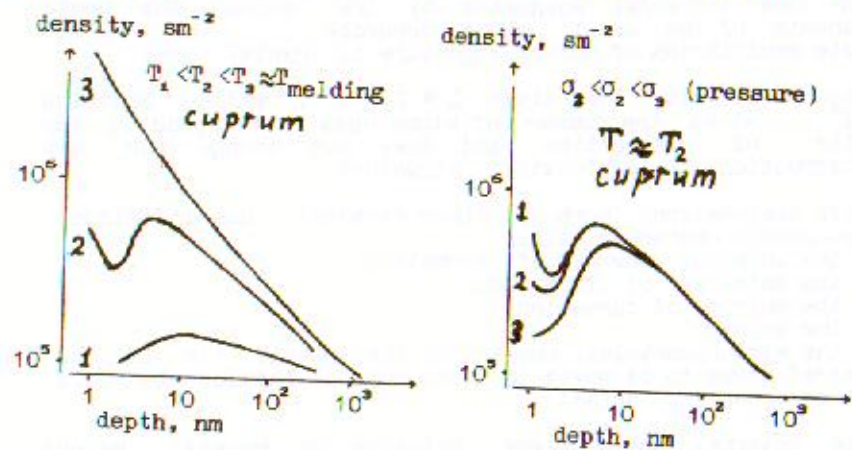
\# The set of defects is limited by the groups of defects with the one-to-one dependence of internal energy on stoichiometrical number or their superposition.

\# Unexcited and by formation of different vacancy type defects excited atoms is indistinguishability, and their position is in crystal lattice indefinable. Gibbs canonical distribution describes the equilibrium distribution of these atoms on energy levels. This statement is inexact for interstitial defects.

The first particular case. The group of circular dislocation loops.

number of loops, sm^{-3} number of loops, sm^{-3}

radius of loops, nm   radius of loops, nm
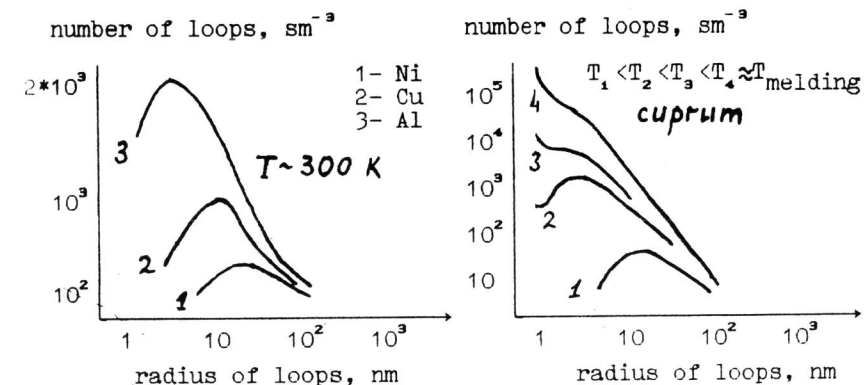
The second particular case. The ensemble of straight edge dislocation

density, sm^{-2}

3

$T_1 < T_2 < T_3 \approx T_{melding}$

cuprum

10^6

2

10^5

1

1 10 10^2 10^3
depth, nm

density, sm^{-2}

$\sigma_2 < \sigma_2 < \sigma_3$ (pressure)

$T \approx T_2$
cuprum

10^6

1

2

3

10^5

1 10 10^2 10^3
depth, nm

The other case consider ensembles of spherical and faceted pores. In general case can be suggested the description of the different types defects interaction, for instance, pores <-> dislocation loops <-> vacances, spherical pores <-> faceted pores, etc.

The results of this estimation describe the density and distribution of defects per size at the different temperature, hydrostatic pressure and the grain sizes. This estimation corresponds to the experimental values of dislocation density in annealing materials and gives the same regularities of crystal dislocation structure. The function of defects distribution per size has maximum, which determined by the elasticity properties of crystal, the type of defect and thermodynamic condition. The dislocation density rises and maximum of distribution function displaces to the small size due to temperature rising. The rising of hydrostatic pressure initiates the decreasing of small sizes defects density.

THE DISLOCATION STRUCTURE OF THE SURFACE.

In the second case it is proposed the thermodynamic interpretation of the surface melting phenomena of the single crystal, which is based on the hypotheses of the connection of the surface melting with the existence at the presurface layer of the crystal the increased density of the defects such as vacancy clusters, dislocations, pores and so on. In the cadre of the equilibrium chemical thermodynamics the calculation of the distribution of defects on function of the depth of the surface layer for the

different temperatures, hydrostatic pressures and the grain sizes have been made. It is shown, that for low temperature the defects distribution have the unimodal form: for the depth about few hundreds interface distances from the surface there is the layer with the increased defects concentration; the amount of defects decreases with the approach to the surface or to the volume of the crystal.The rise of the temperature leads to the expanding of this layer and to the rising of defects density with the displacement of the maximum of defects distribution to the surface. With the further rising of temperature the distribution have the bimodal form - there are two layers of defects: presurface layer and also very thin layer on the surface of crystal. The volume defects concentration in this second layer is higher and it is sufficient high to be amorph or fluid. The surface layer and presurface layer are separated by the crystal region with the small defects density. With the rising of the temperature the width of the both layers increase, the distance between layers decrease and the defects concentration increase. Near the melting temperature the defects distribution change the form again: the bimodal distribution passes to the smooth distribution with the decreasing asymptotic of the defects density with the depth; both the layers are coincided. This transformation are interpreted as the phase transition.

THERMODYNAMICS ESTIMATION OF DISLOCATION DENSITY IN THE NEIGHBORHOOD OF CRACK.

On a reduced thermodynamically conception basis is of great interest the discussion of a cracks-dislocations interaction. The second particular case show the equilibrium defective structure which are formed near by crystal surface. The dislocations accumulation decreases the free energy of crystal. Apparently the analogous effect exists near by crack faces in which structure formation processes can be formed in way different: concentration of defects from a volume; regrouping atoms near walls;dislocations emission from a crack and others. Thermodynamics theory allow that particular mechanisms to pass by. It affirms: the different processes totality must go to free energy decrease, to equilibrium. In the equilibrium establishment outcomes the formation the defective surface layer near crack walls. It modifies the wall surface properties: plasticity, density, microhardness, surface diffusion, surface melting temperature etc. The opposite layers of dislocations interface in the crack edge zone. These dislocations have opposite Burgers vector. The collision of opposite face defects has in the result or a annihilation reaction, or a dislocation loops and dipoles formation. Some theoretical models of crack edge behavior have featured dislocation arrays and plastic effect (Brock,1989; Gao,1989; Ha,1990). The micro mechanisms have suggested in these work are the particle cases going to the equilibrium processes. Ha et.al. (1990) has studied the dis- location-free zone (DFZ) the crack edge in bulk metallic single crystals. The DFZ exists after the stretching and it is not only the

other stretching existed dislocation arrays. Some of these works micro graphs (Ha,1990) show clearly opposite cases: dislocation cluster ahead of the crack edge and the dislocation halo around cracks. Brock and Wu (1989) have analyzed the generation of edge and screw dislocations near the growing and stationary crack. In particular, the crack edge stress can be relaxed, it is thus in effect shielding it from applied loads. The observation can show the evidence for that the dislocation generation process decrease of free energy in crack zone.

The other interesting aspect is in that an internal stress field of formed near crack walls defective layer gives a contribution in total stress field. A role of the contribution can be great in the case of crack evolution and fracture. The showed in the second case result can be prognosticated with some other propositions of crack walls. They are the melting temperature decrease; the amorphous subtle   er formation; the temperature and hydrostatic pressure eff t. These phenomena were observed on free surface of single crystals. (Thernov, 1987)

REFERENCE:

Brock L.M. and Wu J.-S. (1989)   J. Mech. Phys. Solids 37,583.
Fridel J.   (1967)   Dislocations.
Fedoseev V.B.   (1989)   Zurn.Physich.Chimii.V.63.
                                 p.3070.
                       (1990)   Poverhnost.N.7.p.114.
                       (1991)   Abstr.Int.Symp.on calorimetry
                                 and chemical thermodynamic
                                 Moscow,june 23-28.p.203.
Gao H.   (1989)   J. Mech. Phys. Solids 37,583.
Girifalco L.A.   (1975)   Statistical physics of
                                 materials.
Ha K.F., Xu Y.B.,   (1990)   Acta metall. 38,1643.
  Wang X.H. and An Z.Z.
Hirth J.P. and Lothe J. (1972) Theory of dislocations.
Thernov A.A. and   (1987)   Pisjma v GETF.45.130.
  Jacovlev V.A.