# Фазовые превращения и дефекты в кристаллах

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#### ИФТТ РАН, НЦЧ РАН







Черноголовка, где это?

### Черноголовка, вид сверху



### Черноголовка, вид сверху





# Черноголовка, основатели



### Фазовые превращения: -- в объеме -- на внешних и внутренних границах раздела

### -- на внешних поверхностях (огранение-потеря огранки)

### Фазовые превращения:

### Why the facets of surfaces and interfaces appear?

### **Two amorhous phases: smooth interface**



### **Crystal inside of an amorphous phase**



# Equilibrium shape of the crystal surface



**Вульфъ Г.В.** О скорости роста и растворенія кристалловъ *Тр. Варшавск. общ. естествоисп.* 1894–1895. <u>Т. 6.</u> вып. 9. С. 7–11.

Вульфъ Г.В. Къ вопросу о скоростяхъ роста и растворенія кристаллическихъ граней *Изв. Варшавск. ун-та,* 1895 (кн. 7–9). 1896 (кн. 1,2). С. 1–120.

Wulff G. Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen *Zeitschrift für Krystallographie* 1901. Vol. 34. P. 449–530.

# Temperature influence on the equilibrium shape of the surface



### **Temperature influence....**



# **Temperature influence....** NaCI: (100) facets



### $T = 620^{\circ}C$

*T* = 710 °C

J.C. Heyraud, J.J. Mėtois, J. Crystal Growth 84 (1987) 503

Temperature influence on the equilibrium shape of the surface

NaCI: (100) facets

*T* = 710 °C

J.C. Heyraud, J.J. Mėtois, J. Crystal Growth 84 (1987) 503











T = 0  $0 < T < T_{R_3}T_{R_3} < T < T_{R_2}T_{R_2} < T < T_{R_1}T_{R_1} < T < T_{C}$ 

R < 0

R > 0



Lattice gas model with NN and NNN interactions C. Rottman, R. Wortis, *Phys. Rev. B* 29 (1984) 328

### **Temperature influence....**

He<sup>4</sup>: third roughening transition

# T = 0.4 KT = 0.35 K





R.E.Wolf, S. Balibar, *Phys. Rev. Lett.* 51 (1983) 1366

### **Temperature influence....**

### He<sup>3</sup>: (100), (110) and (112) facets

### T = 0.022 K

R. Wagner, S.C. Steel, O.A. Andreeva, R. Jochemsen, G. Frossati. *Phys. Rev. Lett.* 76 (1996) 263



window

(121)

(b)

# Au single crystals at 0.95 T<sub>m</sub>



















# Au single crystal at 0.95 T<sub>m</sub>. Shape discontinuities



# Au single crystal at 0.95 T<sub>m</sub>. Shape discontinuities



# Au single crystal at 0.95 T<sub>m</sub>. Shape discontinuities



# Pb single crystals at 0.97 T<sub>m</sub>. No shape discontinuities



#### J.C. Heyraud, J.J. Metois: Surf. Sci, 128, 334 (1983)

### How the Pb facets grow...



J.C. Heyraud, J.J. Metois: Surf. Sci, 128, 334 (1983)

# Pb single crystal at 0.97 T<sub>m</sub>. No shape discontinuities



#### J.C. Heyraud, J.J. Metois: Surf. Sci, 128, 334 (1983)

# Surfaces of pure metals. Experiment:

- no more than two crystallographically different facets
- facets are isolated and separated by portions of rough surfaces

### **Roughening of Pb surfaces: P-T behaviour**



C. Rottman, R. Wortis, J.C. Heyraud, J.J. Metois. PRL 52 (1984) 1009

### **Rounding near cristal facet**

 $y = A(x - x_c)^{\theta}$  + higher order terms

Andreev theory (mean-field approximation):  $\theta = 2$ Pokrovsky-Talapov theory (including fluctuations):  $\theta = 3/2$ 

A.F. Andreev. *Zh.Eksp.Teor.Fiz.* 79 (1981) 2042 V.L. Pokrovsky, A.L. Talapov. *PRL* 42 (1979) 65 and *Zh.Eksp.Teor.Fiz.* 78 (1980) 269

### **Roughening of Pb surfaces: P-T behaviour**



C. Rottman, R. Wortis, J.C. Heyraud, J.J. Metois. PRL 52 (1984) 1009

Equilibrium crystal shapes in the BCSOS model with enhanced interaction range (a) ECS in the exactly soluble square lattice BCSOS model with stochastic FRE point. (b) ECS with a first-order line extending into the rough area. (c) ECS with first-order facet-to-

(c) ECS with first-order facet-toround boundaries and PTE points.

 (d) ECS with a spontaneous tilted rough phase, i.e., with a <u>first order ridge inside</u> <u>the rough phase</u>.

D. Davidson, M. den Nijs. PRL 84 (2000) 326


#### -- на внутренних границах раздела (огранение-потеря огранки)

Фазовые превращения:

# Low angle grain boundary:





Symmetric tilt boundary, individual lattice dislocations

Reed (1953)

#### Краевая дислокация (edge dislocation)





**Reed (1953)** 

# High angle grain boundary



**Misorientation**,  $\theta \rightarrow$ 

### **Two lattices: coincidence site lattice**



# **Two grains with coincidence site lattice**



## **Two grains with coincidence site lattice**



# **Two amorhous phases: smooth interface**



# **Crystal inside of an amorphous phase**



### **Two crystalline lattices**



# **Two crystalline lattices**



### **Two lattices: coincidence site lattice**



# **Facets in the coincidence site lattice**



# **Facets in the coincidence site lattice**



### **Coincidence sites lattice** $\Sigma$ **3**



# Coincidence sites lattice $\Sigma$ 3 (thick lines) and displacement shift lattice (thin lines)



#### Scheme of Cu bicrystal with coaxial $\Sigma$ 3 GBs



### Cu bicrystal with cylindric $\Sigma 9/\Sigma 3$ GBs



# Section of Cu bicrystal with cylindric $\Sigma 9/\Sigma 3$ GBs, 1020°C, 48 h



# $\Sigma$ 3 tilt GB in Cu, 1020°C (100)<sub>CSL</sub> and 9*R* non-CSL facets (twin plates are not rectangular)



# **Σ3 tilt grain boundary in Cu, 1020°C** (100)<sub>CSL</sub> and 9*R* non-CSL facets



#### **9***R* 82° facet



# Non-CSL 9*R* facet of the $\Sigma$ 3 tilt GB (HRTEM)



Step height 0.58*a*, equal to that of (010)<sub>CSL</sub>

# **Phase diagram for the \Sigma3 GBs in Cu**



# Rectangular facets in Au (100)<sub>CSL</sub> and (010)<sub>CSL</sub> facets



P.J. Goodhew, T.Y. Tan, R.W. Balluffi, Acta Metall. 26 (1978) 557–567

# Σ3 tilt grain boundary in Cu, 800°C (100)<sub>CSL</sub> and 9*R* non-CSL facets

**9***R* 82° facet





# **Phase diagram for the \Sigma3 GBs in Cu**



# Σ3 tilt grain boundary in Cu, 650°C (100)<sub>CSL</sub> and (110)<sub>CSL</sub> facets



# Σ3 tilt grain boundary in Cu, 650°C (100)<sub>CSL</sub> and (130)<sub>CSL</sub> facets



# **Phase diagram for the \Sigma3 GBs in Cu**



# Σ3 tilt grain boundary in Cu, 400°C (100)<sub>CSL</sub> and (010)<sub>CSL</sub> facets



# Σ3 tilt grain boundary in Cu, 400°C (100)<sub>CSL</sub>, (130)<sub>CSL</sub> and (120)<sub>CSL</sub> facets



# **Phase diagram for the \Sigma3 GBs in Cu**



# **Phase diagram for the \Sigma3 GBs in Cu**



# **Σ3 tilt GB in Cu: increase of number of facets with decreasing temperature**

# 800°C

## 400°C



# **Σ3 tilt GB in Cu: increase of number of facets with decreasing temperature**

# 650°C

# **400°C**


# $\Sigma$ 3 and $\Sigma$ 9 grain boundaries in Cu. Experiment:

- By temperature decrease the number of (crystallographically different) facets increases up to six
- The GB facets are not separated by the rough GB portions. The facets form sharp edges.

#### Scheme of Mo bicrystal with coaxial $\Sigma$ 3 GBs



# Shape of $\Sigma$ 3 tilt GB in Mo



# How a facet contacts curved (rough) surface or interface



#### **Roughening of Pb surfaces: P-T behaviour**



C. Rottman, R. Wortis, J.C. Heyraud, J.J. Metois. PRL 52 (1984) 1009

# **Rounding near cristal facet**

 $y = A(x - x_c)^{\theta}$  + higher order terms

Andreev theory (mean-field approximation):  $\theta = 2$ Pokrovsky-Talapov theory (including fluctuations):  $\theta = 3/2$ 

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#### **Roughening of Pb surfaces: P-T behaviour**



C. Rottman, R. Wortis, J.C. Heyraud, J.J. Metois. PRL 52 (1984) 1009



# Shape of $\Sigma$ 3 tilt GB in Mo





Фазовые превращения:

-- на внутренних границах раздела (смачивание)

#### Смачивание внешней поверхности







#### $\sigma_{GB} < 2\sigma_{SL}, \theta > 0$



 $\sigma_{GB} < 2\sigma_{SL}, \theta > 0$ 

Граница зерен в контакте с расплавом устойчива



$$\sigma_{GB} > 2\sigma_{SL}, \ \theta=0$$



Граница зерен в контакте с расплавом устойчива





$$S \qquad \sigma_{SL} \qquad \sigma_{SL} \qquad \sigma_{SL} \qquad \sigma_{GB} \qquad \sigma_{GB}$$

 $\sigma_{GB} > 2\sigma_{SL}, \ \theta=0$ 

Граница зерен в контакте с расплавом неустойчива и должна заменяться жидкой прослойкой

 $\sigma_{GB} < 2\sigma_{SL}, \ \theta > 0$ 

Граница зерен в контакте с расплавом устойчива



Есть системы, в которых такое превращение происходит с повышением температуры



Есть системы, в которых такое превращение происходит с повышением температуры























#### Температура

 $T_w$ 



<u>Система Al-Sn</u> граница наклона <011>{001} θ = 38,5°

С повышением температуры контактный угол понижается, становится равным нулю при 617°С и остается равным нулю при дальнейшем повышении температуры





Вторая (смачивающая) фаза может быть твёрдой

#### Fe–1.3 вес.% C, 915°C, все γ-ГЗ "смочены" Fe<sub>3</sub>C



Выше 905°С все γ-ГЗ "смочены" фазой Fe<sub>3</sub>C



Между 850 и 905°С часть γ-ГЗ "смочена" Fe<sub>3</sub>C



#### Fe–1.3 вес.% C, 885°C, часть γ-ГЗ "смочена" Fe<sub>3</sub>C

![](_page_106_Picture_1.jpeg)

Ниже 850°С нет γ-ГЗ "смоченных" фазой Fe<sub>3</sub>C

![](_page_107_Figure_1.jpeg)
### Fe–1.3 вес.% C, 885°C, часть γ-ГЗ "смочена" Fe<sub>3</sub>C



### Булатная сабля, Стамбул 1656 (Подарок купца И. Булгакова царю Алексею Михайловичу, коллекция Оружейной палаты московского Кремля)



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### Предсмачивание, предплавление







GB segregation: fracture surfaces of Cu–50 at. ppm Bi polycrystals

800°C





GB segregation: fracture surfaces of Cu–100 at. ppm Bi bicrystals

GB 33.2 °<100> 900°C



GB 36.5 °<100> 800°C

### PSEUDOPARTIAL WETTING: BETWEEN COMPLETE AND PARTIAL



### Pseudopartial wetting for grain boundaries=

# AI-30wt.% Zn after HPT: no completely wetted GBs



### AI - 30 wt. % Zn, 5 GPa, 1 rpm, 5 rot



nm

# WC-Co CEMENTED CARBIDES



### Thin GB layer of Co, $\theta = 88^{\circ}$



#### Прикладное значение

- Жидкоподобные равновесные ГЗ прослойки с высокой диффузионной проницаемостью:
   активированное спекание
   охрупчивание ГЗ или катастрофическая электромиграция
- Висмут в припоях для меди: область безопасных концентраций

### Фазовые превращения: -- в объеме под воздействием кручения под высоким давлением

What is severe plastic deformation?

Material is strained, but --it cannot break and --conserves its shape

# **Principle of High Pressure Torsion**



Tool with a sample located within a cavity in a support anvil Tool with cavities in both anvils

## **Principle of Equal Channel Angular Pressing**





## **Principle of Accumulative Roll Bonding**



### **Principle of Cyclic Extrusion and Compression**



## **Principle of Twist Extrusion**



# Severe plastic deformation accelerates diffusion and drives phase transitions:

- Decomposition of supersaturated solid solutions Al–Zn, Cu–Ni, Cu–Co, Cu–Ag
- Formation of supersaturated solid solutions Cu–Co, Cu–Ag
- Crystalline phase → one or two amorphous phases
  NiTi, NdFeB, Ni–Nb–Y
- Amorphous phase → Crystalline phases
  NiFeSiB, FeSiB, CuZrTi...
- fcc-Fe → bcc-Fe, fcc-Co → hcp-Co, αTi↔βTi↔ωTi
  Grain boundary phases

Can we predict, what happens with phases by SPD?

# **Steady-state and grain refinement**



B.B. Straumal et al Scripta Mater 70 (2014) 59

# Steady-state (saturation) during SPD





# Steady-state (saturation) during SPD





# Grain size in steel, "up and down"



Y. Ivanisenko et. al Acta Mater. **51** (2003) 5555 S. Lee, Z. Horita: Mater. Trans. **53** (2012) 38

# Grain size in Ni, "up and down"



R. Pippan et. al Annu. Rev. Mater. Res. 40 (2010) 319

**Diffusive phase transfromations** 

With change of the composition of phases and mass transfer

# Displacive (martensitic) phase transformations

Without change of the composition of phases Without mass transfer Atoms conserve their neighbors Orientation relationships Let us consider pure diffusive Phase transformations

Decomposition of supersaturated solid solutions
 Formation of supersaturated solid solutions

# **Principle of High Pressure Torsion**



Tool with a sample located within a cavity in a support anvil Tool with cavities in both anvils

Does the composition of phases after SPD depend on the composition of phases before SPD??

# What happens, if we deform fully homogenized and fully precipitated alloy???



Mater. Lett. 118 (2014) 111

# What happens, if we deform fully homogenized and fully precipitated alloy???



Mater. Lett. 118 (2014) 111

# What happens, if we deform fully homogenized and fully precipitated alloy???



Mater. Lett. 118 (2014) 111

### Torsion torque reaches steady state after 1.5 rot.



Rotation angle, deg

Mater. Lett. 118 (2014) 111

### Lattice spacing and Co content in Cu-matrix



Mater. Lett. 118 (2014) 111

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Mater. Lett. 118 (2014) 111

Supersaturated solid solution partially decomposes to 2.5 wt.% Co.

Co precipitates partially dissolve in the Cu-based solid solution up to 2.5 wt.% Co in (Cu)

Dissolution and precipitation proceed simultaneous and compete with each other

# What happens, if we deform fully homogenized and fully precipitated alloy???



Mater. Lett. 118 (2014) 111

# What happens, if we deform fully homogenized and fully precipitated alloy???



*T*<sub>eff</sub>= 900°C

Mater. Lett. 118 (2014) 111

Does the composition of phases after SPD depend on the composition of phases before SPD??

No!!!

(equifinality)

### The composition of phases after SPD is as if they were annealed at 900°C

(so called equivalent or effective temperature) SPD-driven mass transfer is equivalent to the bulk diffusion with  $D_{SPD} \sim 10^{-16} \text{ m}^2/\text{s}$ 

Extrapolated bulk diffusion coefficient at 300K is D<sub>SPD</sub> ~ 10<sup>-35</sup> m<sup>2</sup>/s

> Bulk diffusion coefficient at  $T_{eff}$  is  $D_{eff} \sim 10^{-14}$  m<sup>2</sup>/s

The SPD-driven mass transfer is equivalent to the annealing at 900°C

(equivalent or effective temperature)

### Why Teff is equal to 900°C?

### What happens in other Cu-based alloys?

### **Concentration "corridor" in Cu-Ag alloys**



### **Concentration "corridor" in Cu-Sn alloys**



#### Acta Mater. 195 (2020) 184

# Correlation between $T_{eff}$ and activation enthalpy of bulk diffusion of the dopant



## При перемещении в соседний узел атом преодолевает энергетический барьер



# Correlation between $T_{eff}$ and $T_m$ of the dopant



# Correlation between activation enthalpy of bulk diffusion and $T_m$ of the dopant



### Facets in twin GBs in pure Cu after HPT are as if the sample was annealed at 900±50°C







ADEM (2020) 1900589

### If $T_{\rm HPT}$ increases, then $T_{\rm eff}$ decreases



JETP Letters 112 (2020) 37 Письма в ЖЭТФ 112 (2020) 45

## Diffusion- and diffusionless (martensitic) phase transformations

## Ti-Fe alloys αTi↔βTi↔ωTi

#### $\alpha Ti \leftrightarrow \beta Ti \leftrightarrow \omega Ti$ transformations





### $\alpha Ti \leftrightarrow \beta Ti \leftrightarrow \omega Ti$ transformations



[2110]

(a) bcc β-Ti

[110]<sub>6</sub> (222)

[2110]

[101]<sub>8</sub>

Acta Mater. 144 (2018) 337

### $\alpha Ti \leftrightarrow \beta Ti \leftrightarrow \omega Ti$ transformations



#### Best fit between $\beta$ Ti and $\omega$ Ti phases is at 4 wt. % Fe

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### Conclusions

1. Composition of phases after HPT does not depend on that before HPT. It is, therefore, equifinal. 2. It is equal to that after equibrium annealing at certain  $T_{\rm eff}$ . 3. Reason: high steady-state concentration of lattice defects in dynamic equilibrium 4.  $T_{\rm eff} \sim (T_{\rm m} \text{ and } Q_{\rm b})$  of the dopant 5. Diffusion- and diffusionless (martensitic) phase transformations

### Фазовые превращения:

-- на внутренних границах раздела