

Магние́вые сплавы: назначение, свойства и управление ими

Дмитрий Орлов

Ritsumeikan Global Innovation Research Organisation,
Ritsumeikan University,
Japan

03 декабря 2012

Содержание доклада

- Магний и его сплавы: сопоставление с другими материалами и потенциальные применения;
- Проблемы при разработке технологий получения изделий из магниевых сплавов;
- Ключевые элементы управления свойствами магниевых сплавов:
 - Кристаллическая решетка магния, механизмы и типичные текстуры деформации;
 - Текстуры металлических материалов (*справка*)
 - Потребность в введении такого параметра;
 - Основные понятия и методы анализа;
 - Отображение и использование информации;
 - Легирование, фазы и морфология интерметаллидов;
- Управление свойствами в магниевых сплавах на примере ЗК60;
- Новый проект

Магний и его сплавы

сопоставление с другими
материалами

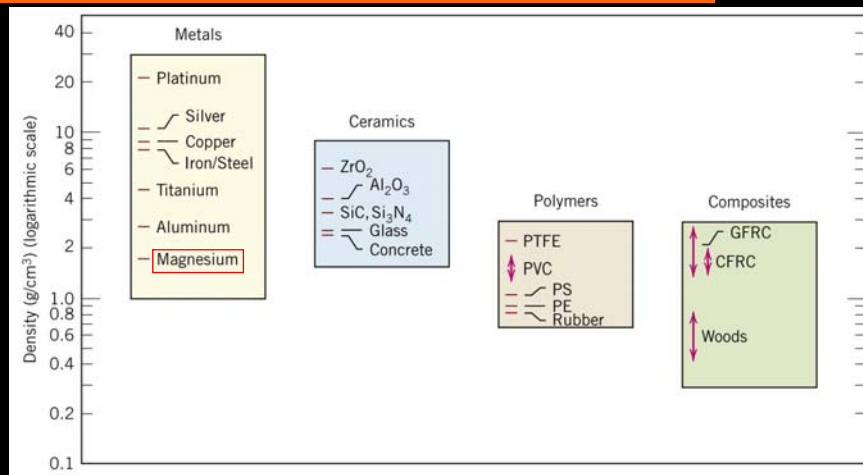
Историческая справка



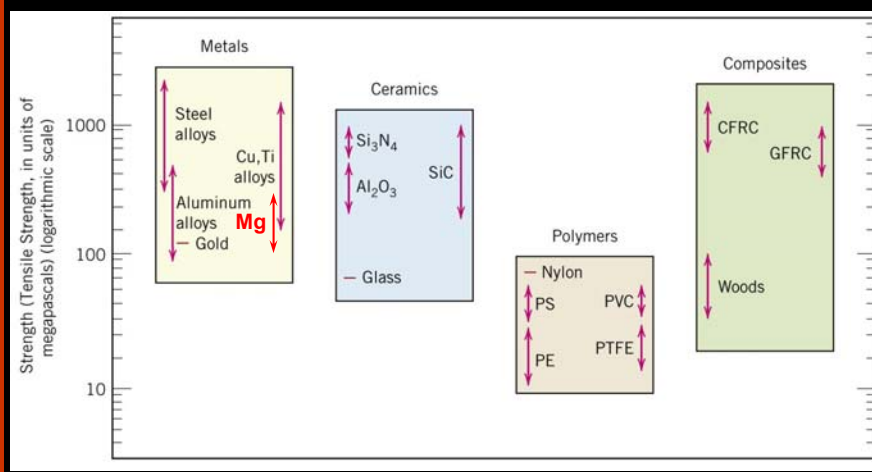
• Materials drive our society

- Stone Age
- Bronze Age
- Iron Age
- Now?
 - Magnesium Age?
 - Polymer Age?
 - Silicon Age?

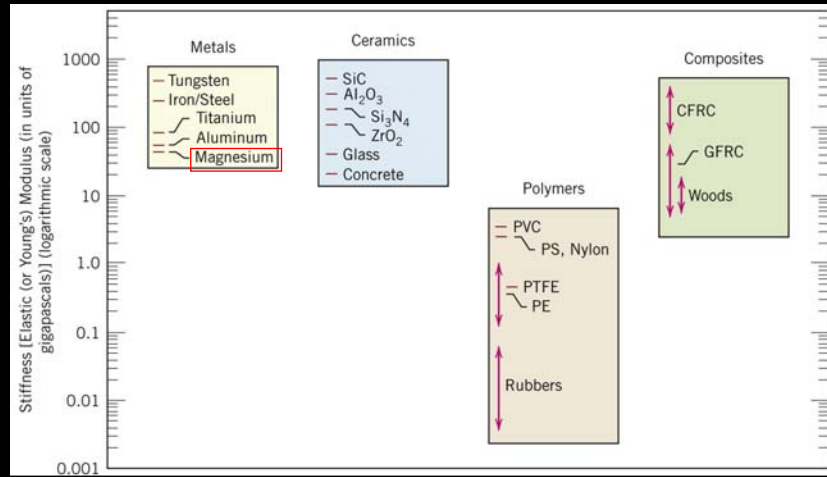
Плотность



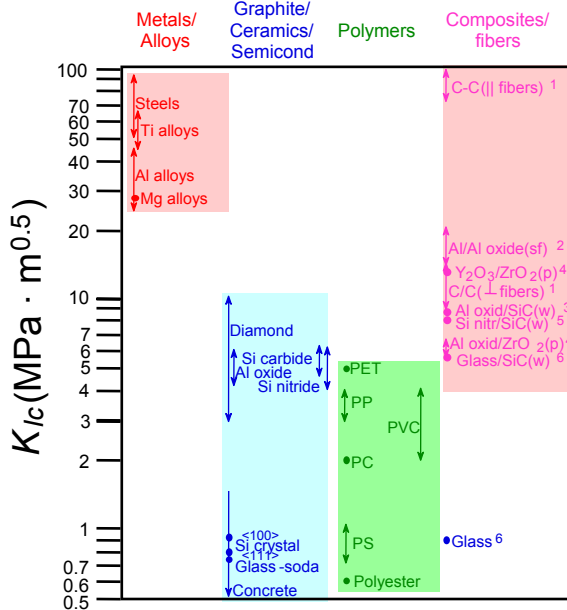
Прочность



Жесткость



Fracture Toughness

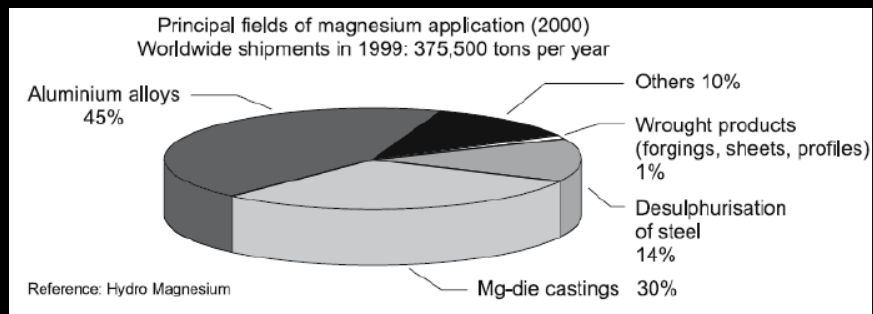


Based on data in Table B.5, Callister & Rethwisch 8e.

Composite reinforcement geometry is: f = fibers; sf = short fibers; w = whiskers; p = particles. Addition data as noted (vol. fraction of reinforcement):

- (55vol%) ASM Handbook, Vol. 21, ASM Int., Materials Park, OH (2001) p. 606.
- (55 vol%) Courtesy J. Cornie, MMC, Inc., Waltham, MA.
- (30 vol%) P.F. Becher et al., *Fracture Mechanics of Ceramics*, Vol. 7, Plenum Press (1986), pp. 61-73.
- Courtesy CoorsTek, Golden, CO.
- (30 vol%) S.T. Buljan et al., "Development of Ceramic Matrix Composites for Application in Technology for Advanced Engines Program", ORNL/Sub/85-22011/2, ORNL, 1992.
- (20vol%) F.D. Gace et al., *Ceram. Eng. Sci. Proc.*, Vol. 7 (1986) pp. 978-82.

Использование



Магний и его сплавы

потенциальные применения

Make our society more sustainable through...

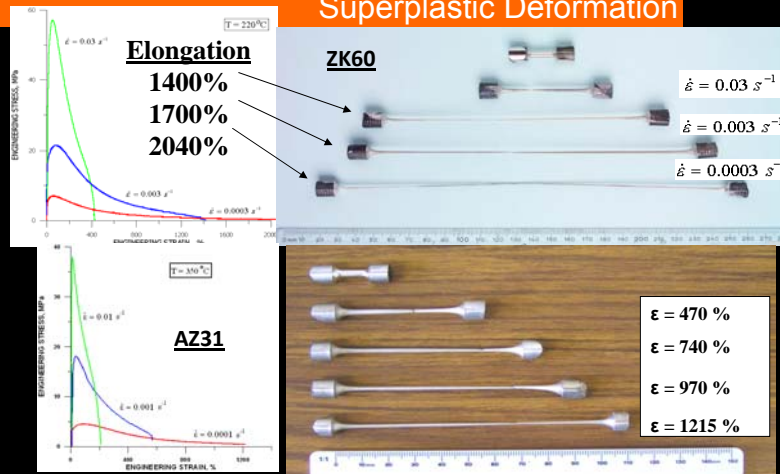
- Higher structural efficiency:
 - LIGHTER VEHICLES →
 - → less material to construct;
 - → less fuel to move;
 - → improved energy absorption in collisions (safety)

Make our society more sustainable through...

- Improved functional properties:
 - NEW HORIZONS FOR DEVICES AND APPLICATIONS →
 - → Metals for hydrogen storage;
 - → 'Clean' and bio-resorbable implants;
 - → Up to your imagination...

Ultra-fine grained Mg for...

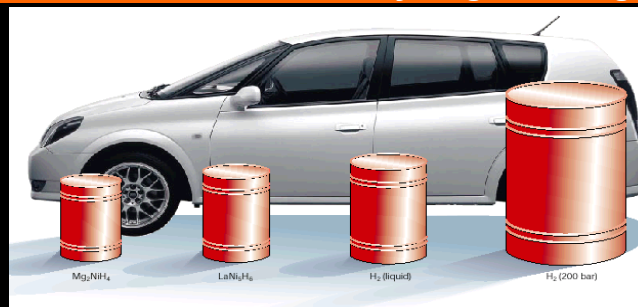
Superplastic Deformation



(The slide materials are a courtesy of Prof Yuri Estrin, Monash University, Australia)

Mg can be a material for...

Hydrogen Storage

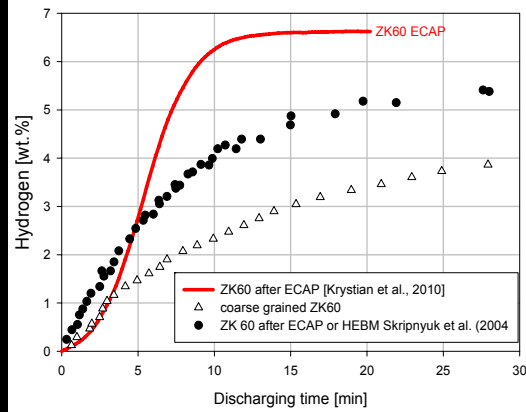


- The automotive industry demands:
- at least 6-7 wt.% of H_2 in hydride;
 - H_2 should be released below 200 C;
 - Fast desorption kinetics

(The slide materials are a courtesy of Prof Yuri Estrin, Monash University, Australia)

Example

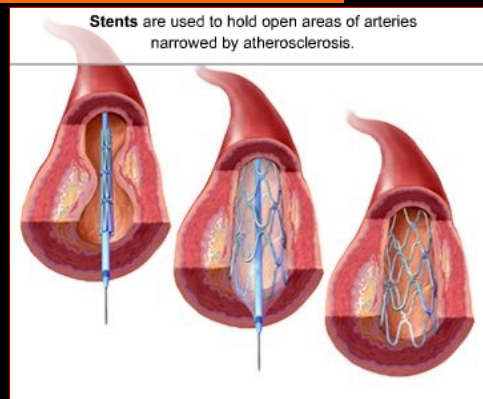
In Mg alloy ZK60



(The slide materials are a courtesy of Prof Yuri Estrin, Monash University, Australia)

Mg can be a material for...

Vascular stents



Requirements:

- Strength $\propto 1/\sqrt{\text{GRAIN SIZE}}$
- Reproducibility of properties

→ *Ultrafine granularity*

(The slide materials are a courtesy of Prof Yuri Estrin, Monash University, Australia)

Изделия из магниевых сплавов

- Проблемы при разработке технологий получения:
 - Низкая технологическая пластичность
- Возможный путь решения:
 - Литье конечных изделий;
 - Создание процессов деформационной обработки с преобладанием всестороннего сжатия в схеме нагружения;
 - Управление текстурой

Изделия из магниевых сплавов

- Проблемы при разработке технологий получения:
 - Низкая прочность
- Возможный путь решения:
 - Легирование;
 - Измельчение структуры;
 - Управление текстурой

Изделия из магниевых сплавов

- Проблемы при разработке технологий получения:
 - Низкая коррозионная стойкость
- Возможный путь решения:
 - Нанесение защитных покрытий;
 - Легирование для улучшения коррозионной стойкости по всему объему;
 - Использование эффекта

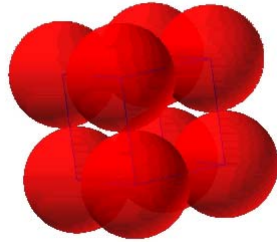
Магний и его сплавы

кристаллография и механизмы деформации

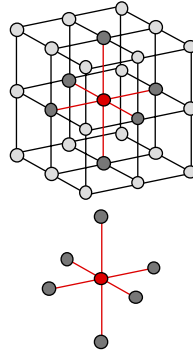
Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- **Close-packed directions** are cube edges.

- **Coordination # = 6**
(# nearest neighbors)



(Courtesy P.M. Anderson)

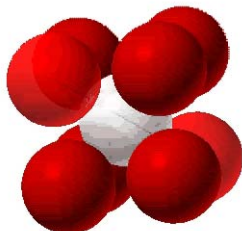


Body Centered Cubic Structure (BCC)

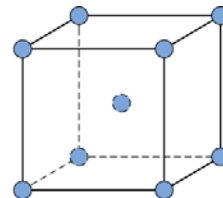
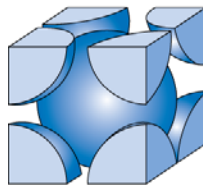
- Atoms touch each other along cube diagonals.
--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- **Coordination # = 8**



(Courtesy P.M. Anderson)



Adapted from Fig. 3.2,
Callister & Rethwisch 8e.

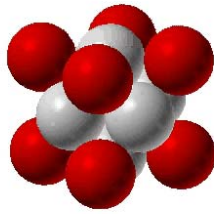
2 atoms/unit cell: 1 center + 8 corners x 1/8

Face Centered Cubic Structure (FCC)

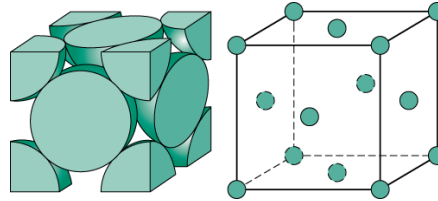
- Atoms touch each other along face diagonals.
- Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12



(Courtesy P.M. Anderson)

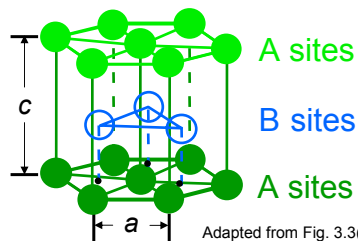


Adapted from Fig. 3.1, Callister & Rethwisch 8e.

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

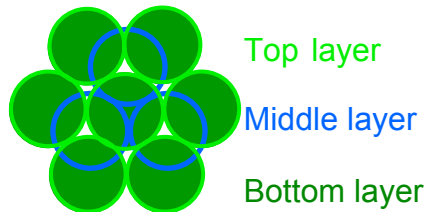
Hexagonal Close-Packed Structure (HCP)

- 3D Projection



Adapted from Fig. 3.3(a), Callister & Rethwisch 8e.

- 2D Projection



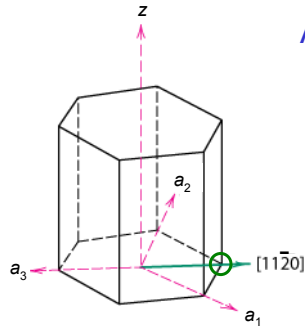
- Coordination # = 12

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

- $c/a = 1.633$

HCP Crystallographic Directions



Adapted from Fig. 3.8(a),
Callister & Rethwisch 8e.

ex: $\frac{1}{2}, \frac{1}{2}, -1, 0$

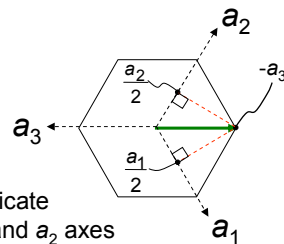
Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1 , a_2 , a_3 , or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvw]$

dashed red lines indicate
projections onto a_1 and a_2 axes

$\Rightarrow [11\bar{2}0]$



HCP Crystallographic Directions

• Hexagonal Crystals

- 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., $u'v'w'$) as follows.

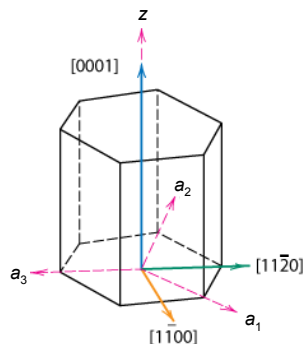


Fig. 3.8(a), Callister & Rethwisch 8e.

$$[u'v'w'] \rightarrow [uvw]$$

$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

$$t = -(u + v)$$

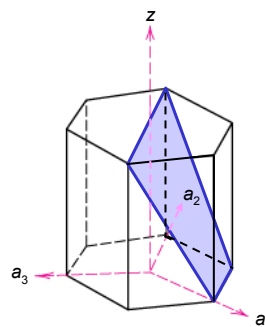
$$w = w'$$

Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.
- Algorithm
 1. Read off intercepts of plane with axes in terms of a , b , c
 2. Take reciprocals of intercepts
 3. Reduce to smallest integer values
 4. Enclose in parentheses, no commas i.e., (hkl)

Crystallographic Planes (HCP)

<u>example</u>	a_1	a_2	a_3	c
1. Intercepts	1	∞	-1	1
2. Reciprocals	1	$1/\infty$	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1
4. Miller-Bravais Indices	$(10\bar{1}1)$			

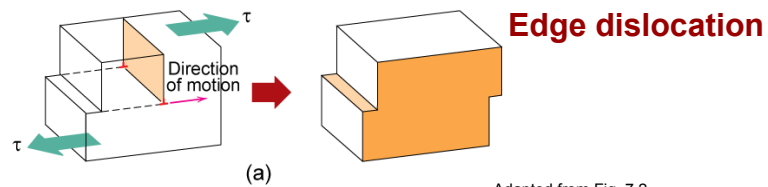


Adapted from Fig. 3.8(b),
Callister & Rethwisch 8e.

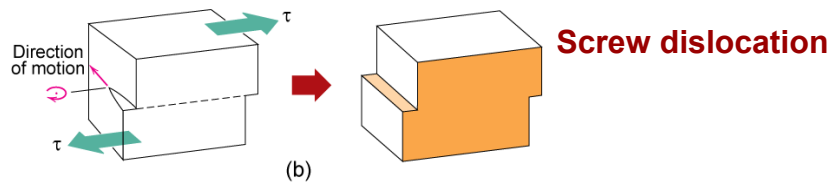
Possible Deformation Mechanisms

Dislocation slip:

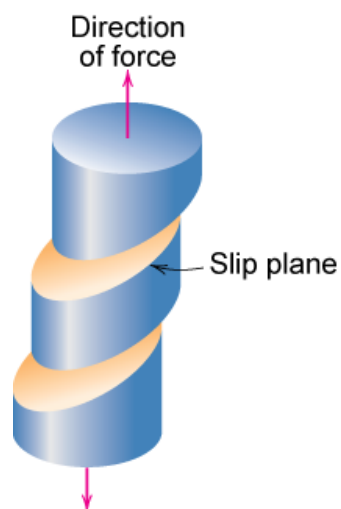
- A dislocation moves along a **slip plane** in a **slip direction** perpendicular to the dislocation line
- The slip direction is the same as the **Burgers vector** direction



Adapted from Fig. 7.2,
Callister & Rethwisch 8e.



Single Crystal Slip



Adapted from Fig. 7.8,
Callister & Rethwisch 8e.

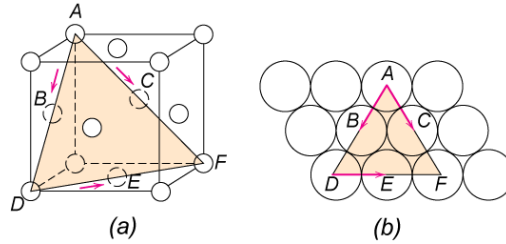
Adapted from Fig.
7.9, Callister &
Rethwisch 8e.



Deformation Mechanisms

Slip System

- Slip plane - plane on which easiest slippage occurs
 - Highest planar densities (and large interplanar spacings)
- Slip directions - directions of movement
 - Highest linear densities



Adapted from Fig. 7.6, Callister & Rethwisch 8e.

- FCC Slip occurs on $\{111\}$ planes (close-packed) in $\langle 110 \rangle$ directions (close-packed)
 - => total of 12 slip systems in FCC
- For BCC & HCP there are other slip systems.

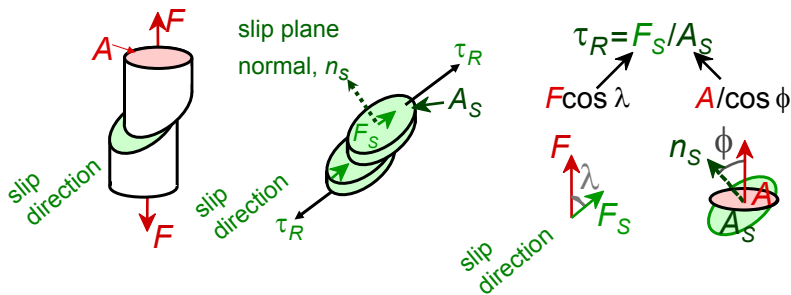
Stress and Dislocation Motion

- Resolved shear stress, τ_R
 - results from applied tensile stresses

Applied tensile stress: $\sigma = F/A$

Resolved shear stress: $\tau_R = F_S/A_S$

Relation between σ and τ_R



$$\tau_R = \sigma \cos \lambda \cos \phi$$

Critical Resolved Shear Stress

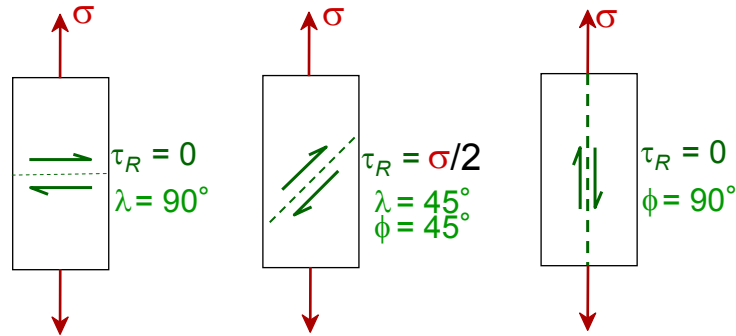
- Condition for dislocation motion:

$$\tau_R > \tau_{CRSS}$$

- Ease of dislocation motion depends on crystallographic orientation

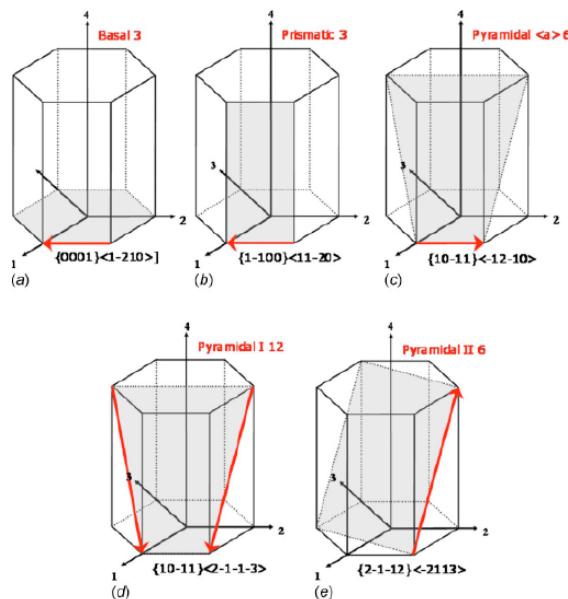
↑
typically
 10^{-4} GPa to 10^{-2} GPa

$$\tau_R = \sigma \cos \lambda \cos \phi$$



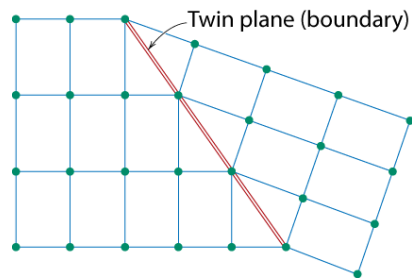
τ maximum at $\lambda = \phi = 45^\circ$

Dislocation slip systems in Mg



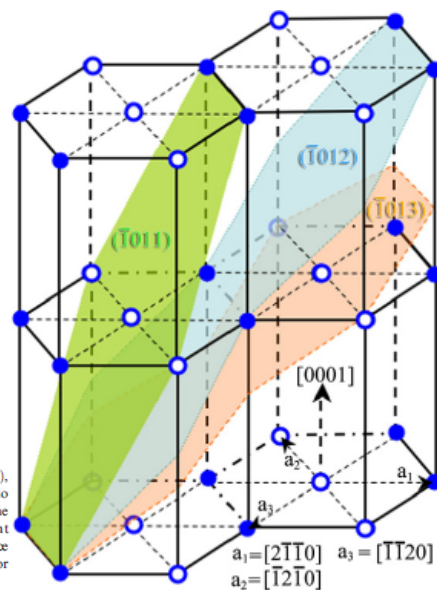
Possible Deformation Mechanisms

- TWINNING
- Twin boundary (plane)
 - Essentially a reflection of atom positions across the twin plane.



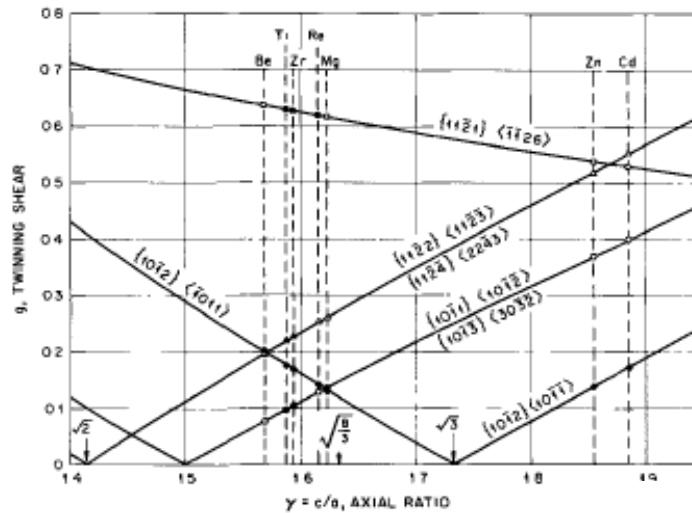
Adapted from Fig. 4.9,
Callister & Rethwisch 8e.

Twinning in Mg



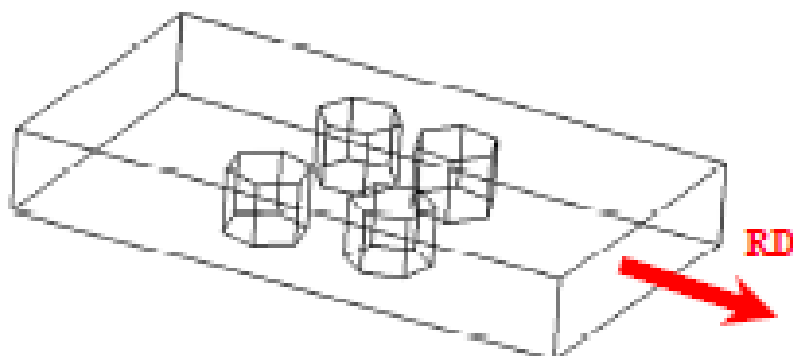
An hcp crystal lattice showing three twinning planes, $(\bar{1}011)$, $(\bar{1}012)$ and $(\bar{1}013)$, which share the common zonal axis parallel to $[\bar{1}2\bar{1}0]$. Atoms are represented with solid circles in A-type $(\bar{1}2\bar{1}0)$ plane and empty circles in B-type $(\bar{1}2\bar{1}0)$ plane. The spacing between adjacent A-type and B-type $(\bar{1}2\bar{1}0)$ planes is equal to $a/2$, where a is the lattice constant. The intermediate basis layers of the hcp crystal are omitted for clarity.

Direction of twinning in HCP metals



Variation of twinning shear with the axial ratio. For hexagonal metals, a filled symbol indicates that the twin mode is active.

Typical rolling texture of Mg

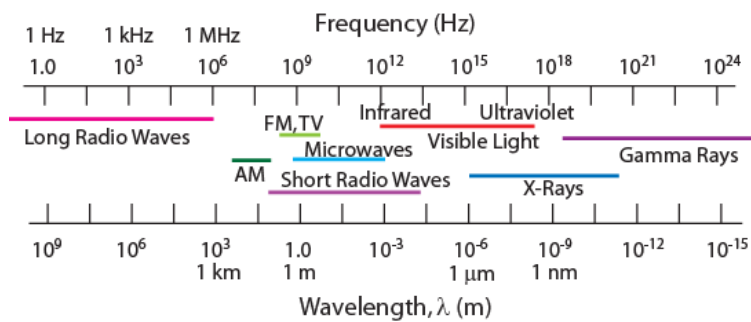


справка

текстуры металлических материалов

X-Ray Diffraction

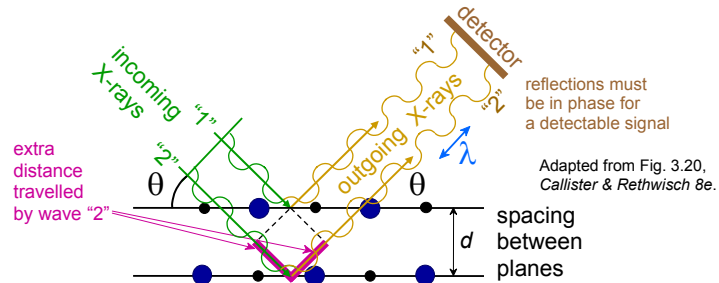
Electromagnetic Spectrum



- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

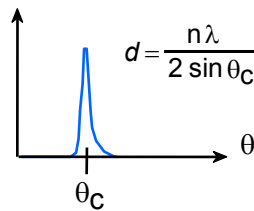
X-Rays to Determine Crystal Structure

- Incoming X-rays **diffract** from crystal planes.

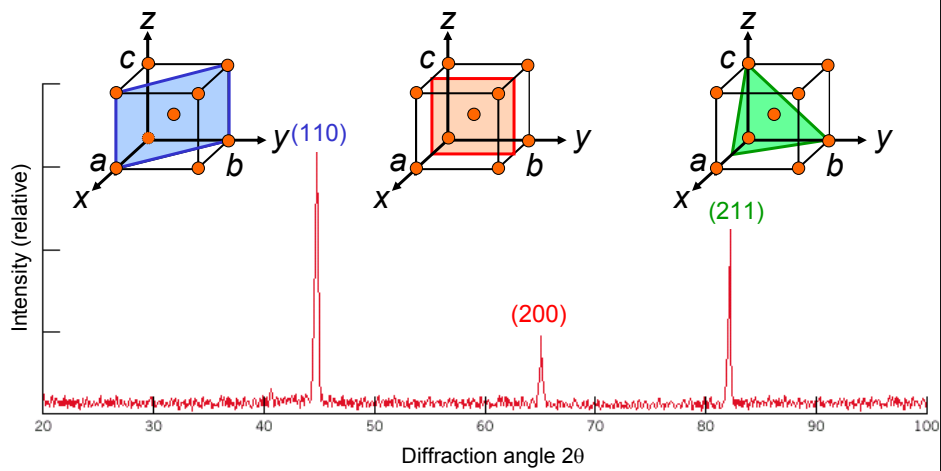


Measurement of critical angle, θ_c , allows computation of planar spacing, d .

X-ray intensity (from detector)

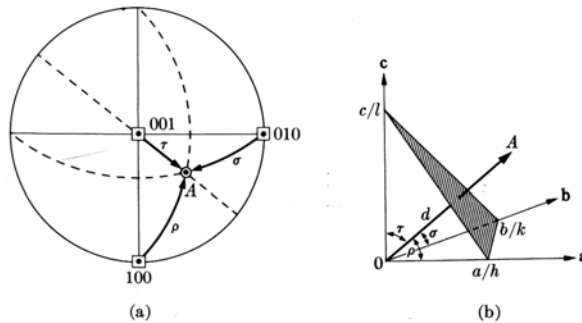


X-Ray Diffraction Pattern



Miller indices of a pole

Miller indices are a convenient way to represent a **direction** or a **plane normal** in a crystal, based on **integer multiples** of the **repeat distance** parallel to each axis of the **unit cell** of the **crystal lattice**. This is simple to understand for cubic systems with equiaxed Cartesian coordinate systems but is more complicated for systems with lower crystal symmetry. **Directions** are simply defined by the set of multiples of lattice repeats in each direction. **Plane normals** are defined in terms of **reciprocal** intercepts on each axis of the unit cell.



When a plane is written with parentheses, (hkl) , this indicates a particular plane normal: by contrast when it is written with curly braces, $\{hkl\}$, this denotes a family of planes related by the crystal symmetry. Similarly a direction written as $[uvw]$ with square brackets indicates a particular direction whereas writing within angle brackets, $\langle uvw \rangle$ indicates the family of directions related by the crystal symmetry.

Fig. 2-39 Determination of the Miller indices of a pole.

The Stereographic Projection

- Uses the inclination of the normal to the crystallographic plane: the points are the intersection of each crystal direction with a (unit radius) sphere

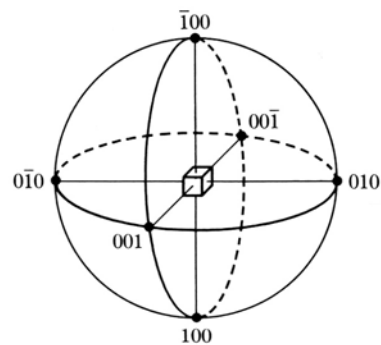


Fig. 2-25 $\{100\}$ poles of a cubic crystal.

Projection from Sphere to Plane

- Projection of spherical information onto a flat surface
 - Equal area projector (Schmid projection)
 - Equiangular projectic (Wulff projection, more common in crystallography)

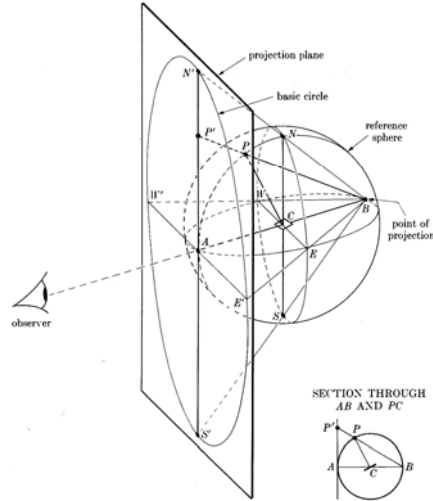
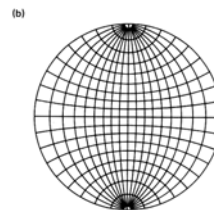
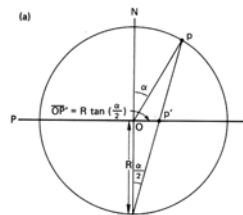


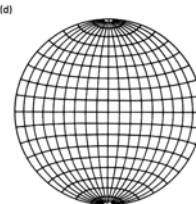
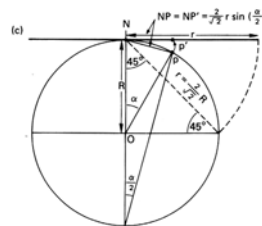
Fig. 2-27 The stereographic projection.

Stereographic, Equal Area Projections

Stereographic
(Wulff)
Projection*:
 $OP' = R \tan(\theta/2)$

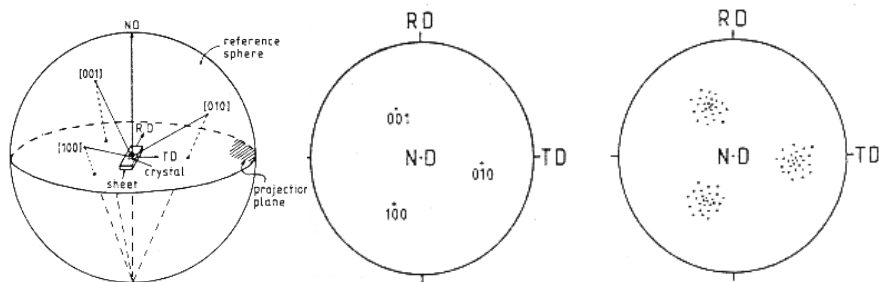


Equal Area
(Schmid)
Projection:
 $OP' = R \sin(\theta/2)$



Pole Figure Example

- If the goniometer is set for $\{100\}$ reflections, then all directions in the sample that are parallel to $\langle 100 \rangle$ directions will exhibit diffraction. The example shows a crystal oriented to put all 3 $\langle 100 \rangle$ directions approximately equally spaced from the ND.

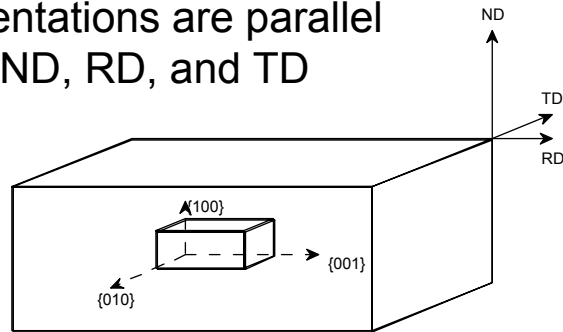


Miller Index Definition of a Crystal Orientation

- We use a set of three orthogonal directions as the reference frame. Mathematicians set up a set of **unit vectors** called e_1 , e_2 and e_3 .
- In many cases we use the names Rolling Direction (RD) $\parallel e_1$, Transverse Direction (TD) $\parallel e_2$, and Normal Direction (ND) $\parallel e_3$.
- We then identify a crystal (or plane normal) parallel to 3rd axis (ND) and a crystal direction parallel to the 1st axis (RD), written as $(hkl)[uvw]$.

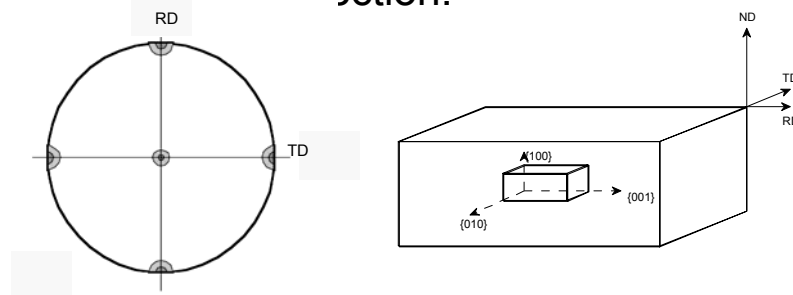
Cube Texture (100)[001]: cube-on-face

- Observed in recrystallization of *fcc* metals
- The 001 orientations are parallel to the three ND, RD, and TD directions.

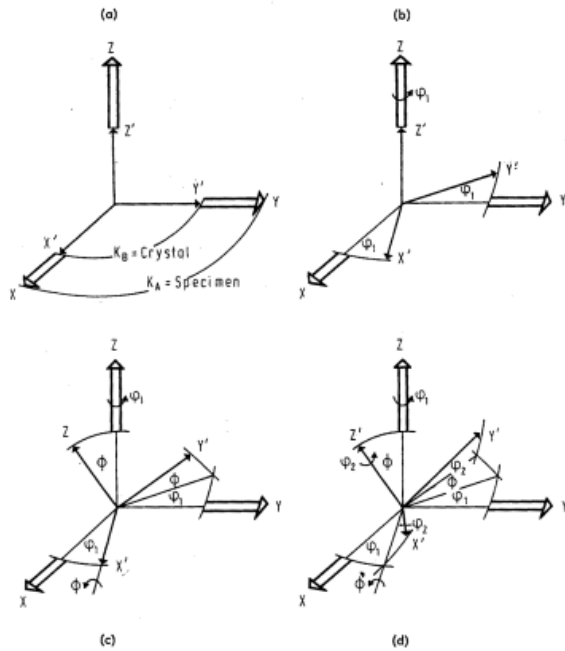


Sharp Texture (Recrystallization)

- Look at the (001) pole figures for this type of texture: maxima correspond to {100} poles in the standard stereographic projection.

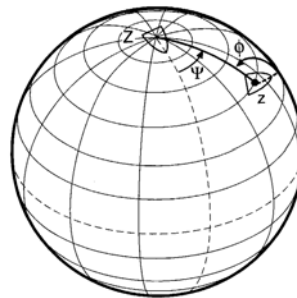


(Bunge) Euler Angle Definition



Euler Angles, Ship Analogy

- Analogy: position and the heading of a boat with respect to the globe. *Latitude* (θ) and *longitude* (ψ) describe the position of the boat; third angle describes the *heading* (ϕ) of the boat relative to the line of longitude that connects the boat to the North Pole.

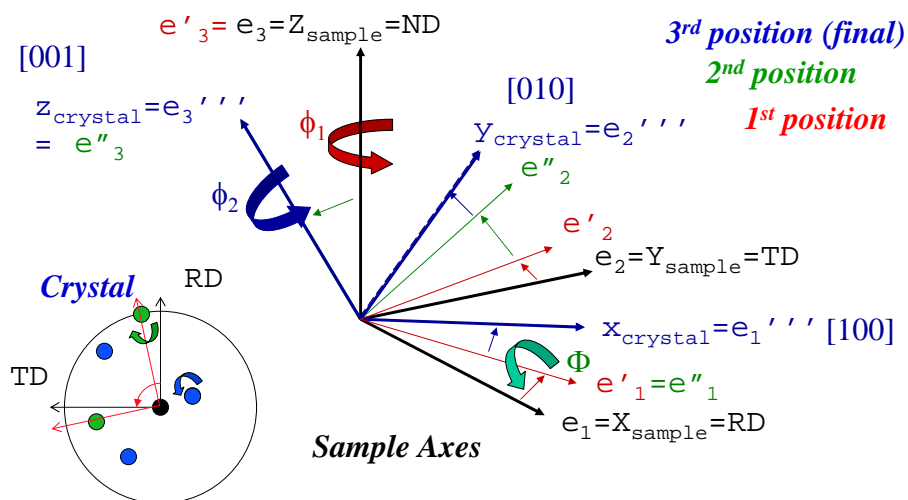


Kocks vs. Bunge angles:
to be explained later!

Meaning of Euler angles

- The first two angles, ϕ_1 and Φ , tell you the position of the [001] crystal direction relative to the specimen axes.
- Think of rotating the crystal about the ND (1st angle, ϕ_1); then rotate the crystal out of the plane (about the [100] axis, Φ);
- Finally, the 3rd angle (ϕ_2) tells you how much to rotate the crystal about [001].

Euler Angles, Animated



Complete orientations in the Pole

Note the loss of information in a diffraction experiment if each set of poles from a single component cannot be related to one another.

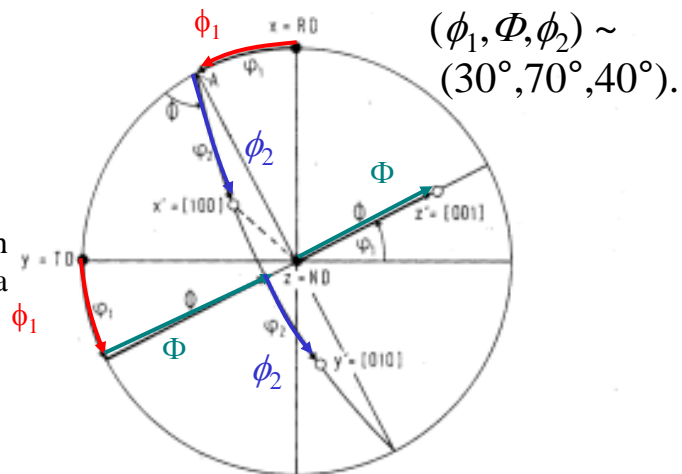
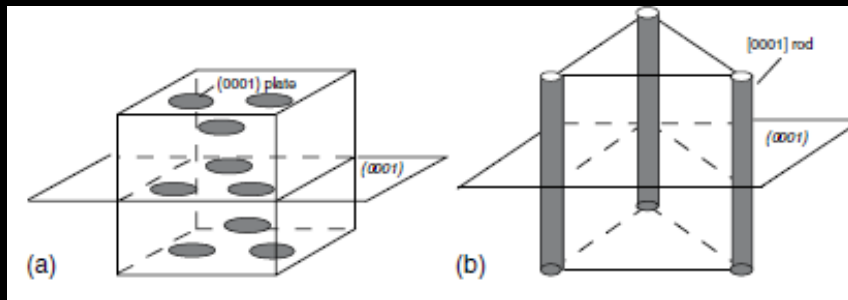


Figure 2.22 The orientation of the crystal directions $X' = [100]$, $Y' = [010]$, $Z' = [001]$ in the stereographic projection in the simple coordinate system (pole figure) expressed by the Euler angles $\varphi_1, \Phi, \varphi_2$.

Магний и его сплавы

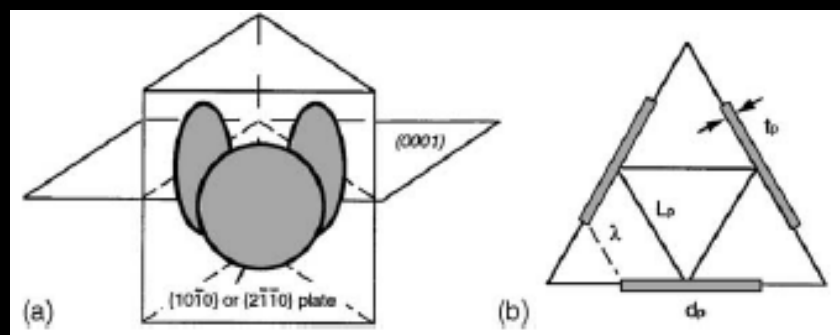
Морфология интерметаллидов

Possible precipitate shapes in Mg alloys



[Nie, Scr.Mat. (2003)]

Possible precipitate shapes in Mg alloys

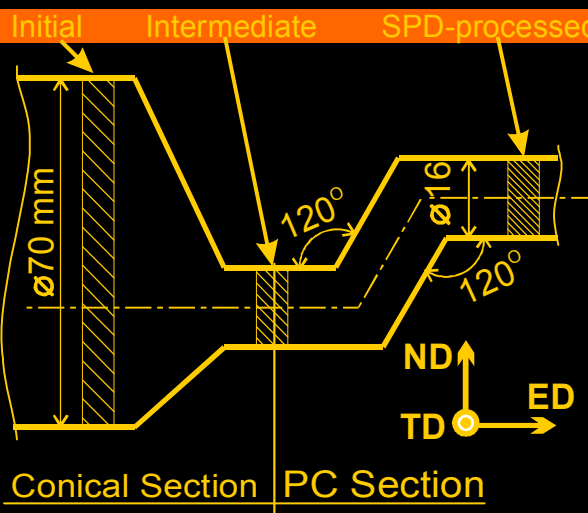


[Nie, Scr.Mat. (2003)]

Integrated extrusion and ECAP

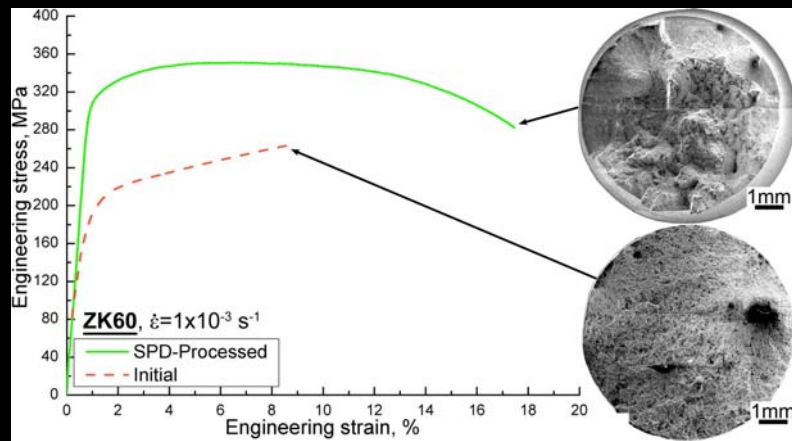
to improve performance
of magnesium alloy
ZK60

Scheme of Integrated Extrusion and ECAP



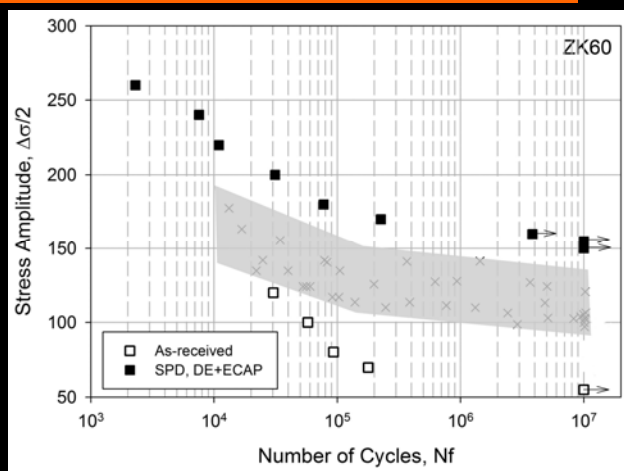
[Orlov et al,
Acta.Mat. (2011)]

Mg ZK60, Tensile Property Performance



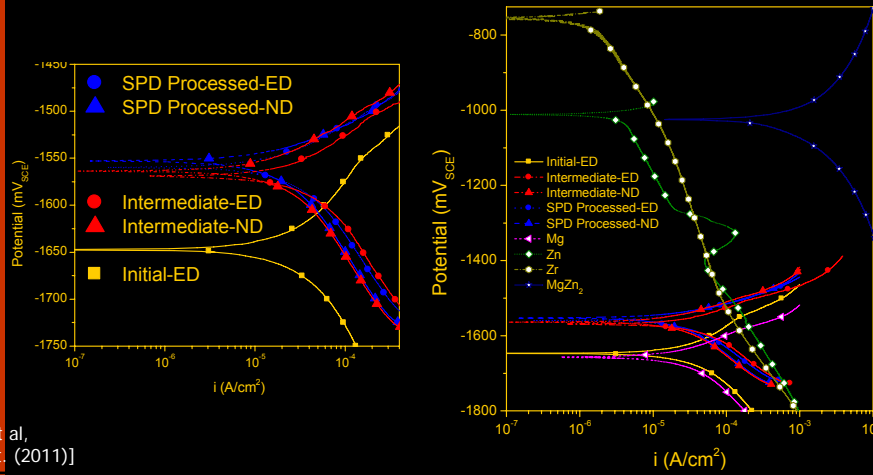
[Orlov et al, Acta.Mat. (2011)]

Mg ZK60, Fatigue Performance



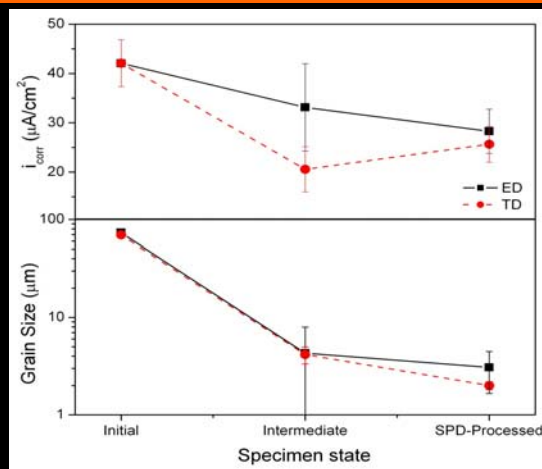
[Vinogradov et al, Scr.Mat. (2012)]

Mg ZK60, Corrosion Performance



[Orlov et al, Acta.Mat. (2011)]

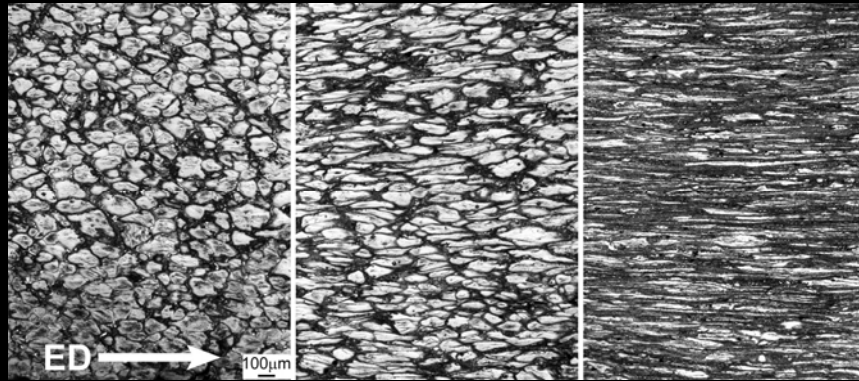
Mg ZK60, Corrosion Performance



[Orlov et al, Acta.Mat. (2011)]

Mg ZK60, Microstructure Evolution by LOM

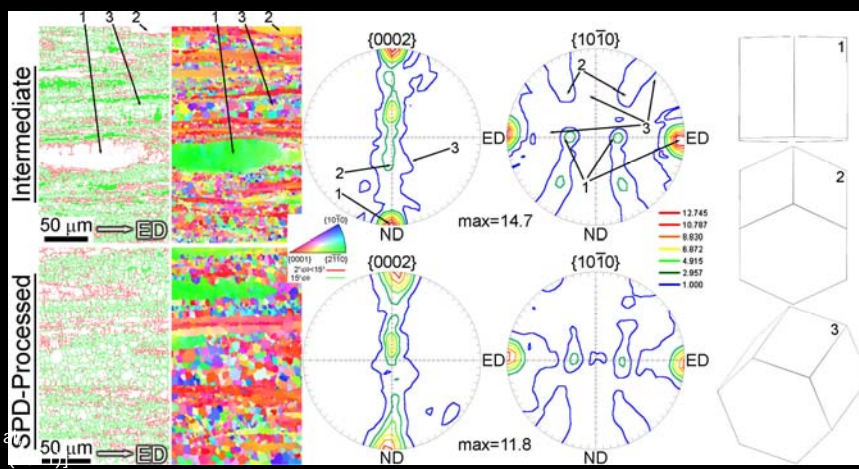
along conical section of the die



[Orlov et al,
Acta.Mat. (2011)]

Mg ZK60, Microstructure Evolution by EBSD

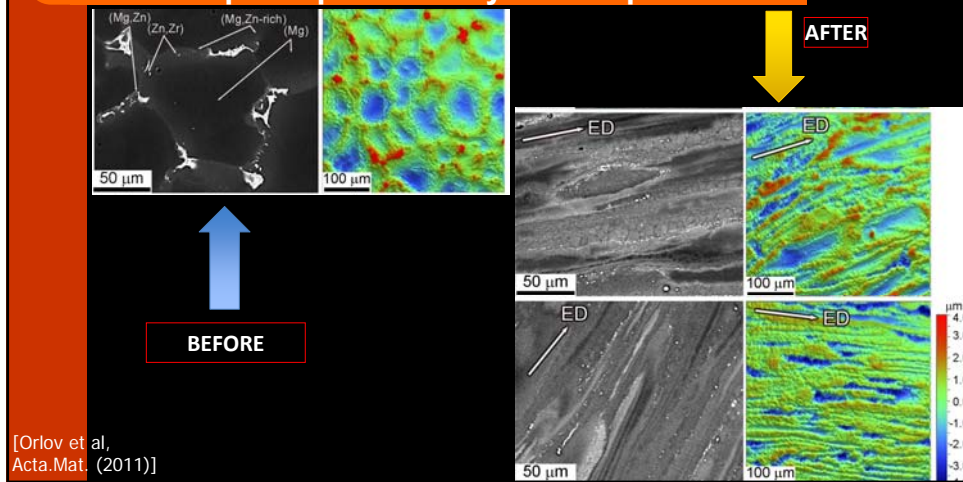
in PC section of the die



[Orlov et al,
Acta.Mat. (2011)]

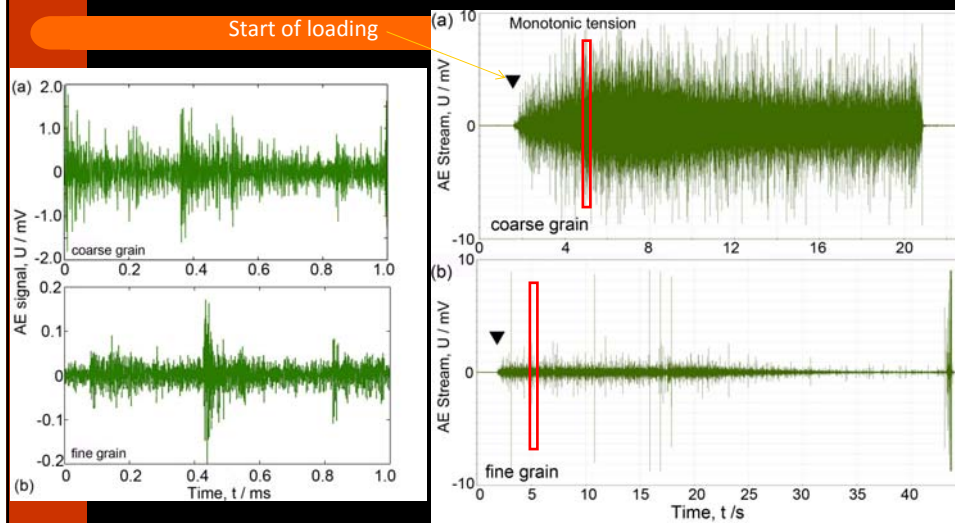
Mg ZK60, Intermetallics Evolution by SEM

and optical profilometry after exposure test



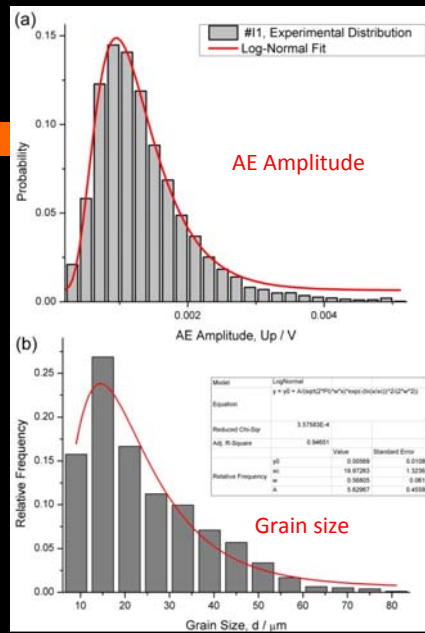
AE in Mg ZK60 Alloy

Start of loading



Correlation between the AE amplitude and grain size

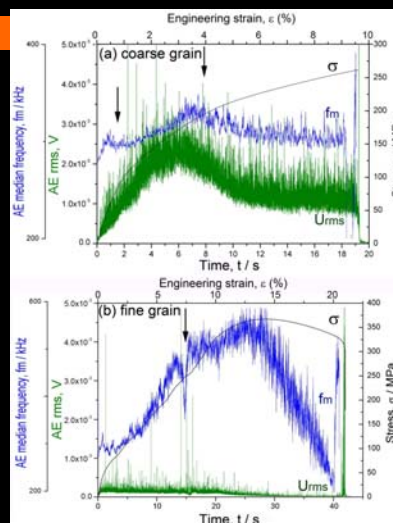
- Both obey log-normal distribution



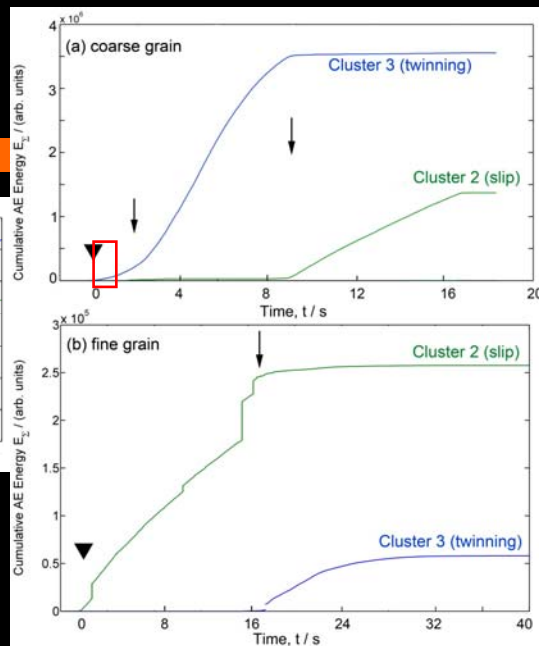
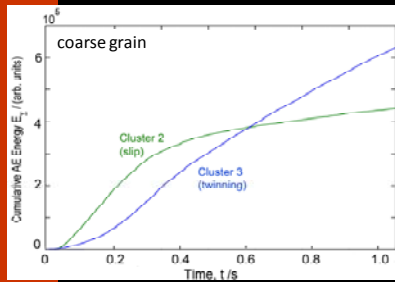
Mg ZK60, AE rms and median frequency

As received

After integrated extrusion



Evolution of AE cluster members



Summary

- Four-meter long bars were manufactured by integrated extrusion and equal channel angular pressing.
- Tensile, fatigue and corrosion properties were simultaneously improved by such processing.
- Corrosion property is controlled by particles redistribution, while mechanical properties depend primarily on microstructure and texture evolution.

Новый проект: цели

- Изучить механизмы деформации в магниевых сплавах используя АЭ и EBSD анализ как основные инструменты;
- Понять параметры обработки и структурного состояния магниевых сплавов определяющие механизмы деформации;
- Научиться управлять механическими и функциональными свойствами магниевых сплавов

Thank you for attention!