Massachusetts Institute of Technology
Harvard Medical School
Brigham and Women's/Massachusetts General Hosp.
VA Boston Healthcare System

2.79J/3.96J/BE.441/HST522J

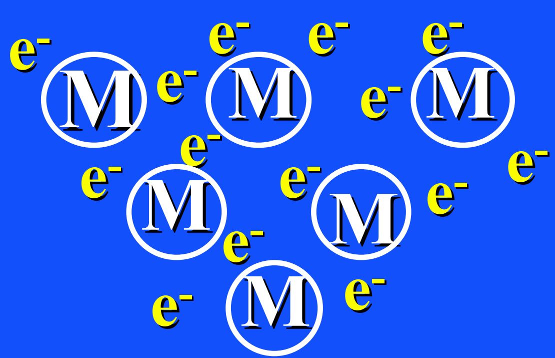
MATERIALS: BONDING AND PROPERTIES

M. Spector, Ph.D.

CHEMICAL BONDING

Primary	
• Metallic	100 kcal/mol
• Covalent	200
• Ionic	10-20
Secondary	
• van der Waals	1-2
• Hydrogen	3-7
• Hydrophobic Interactions	1-2

MATERIALS WITH PRIMARY ATOMIC BONDS

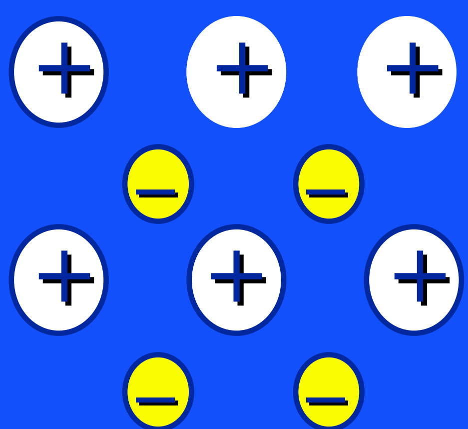


Metallic

(electron "glue" or "cloud")

-metals

-100 kcal/mol



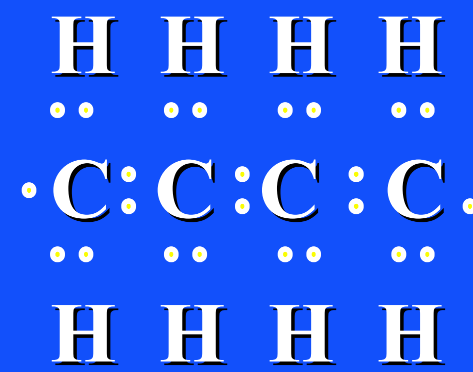
Ionic

(attraction of positive and negative ions)

-ceramics

-calcium phosphates

-10-20 kcal/mol



Covalent

(shared- pair electrons)

-polymers

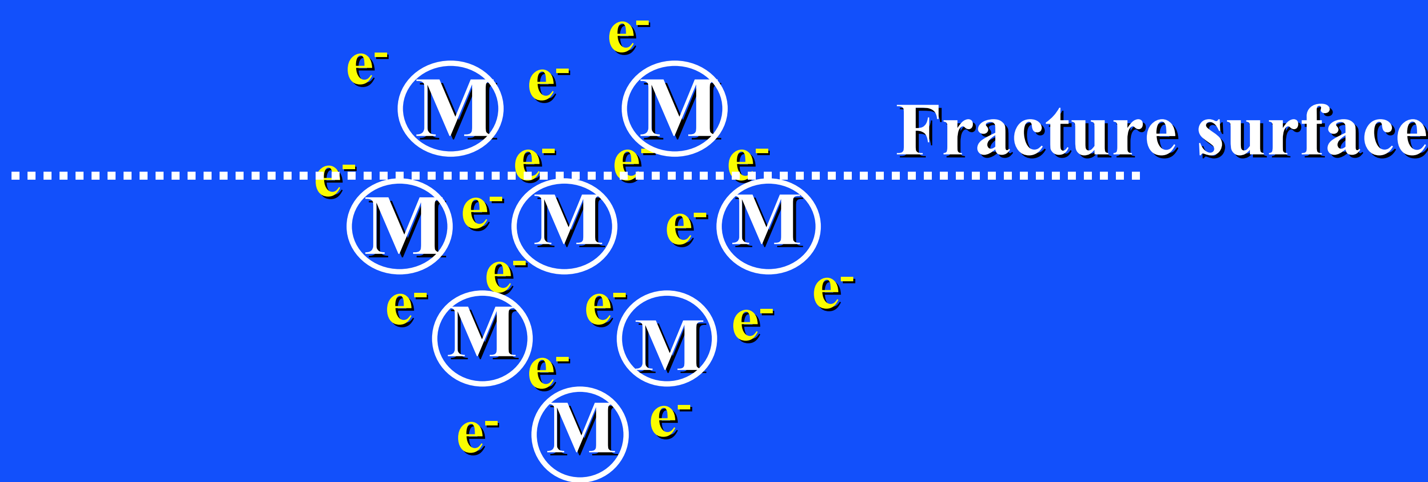
-biological macromolec. (*e.g.*, proteins)

-200 kcal/mol

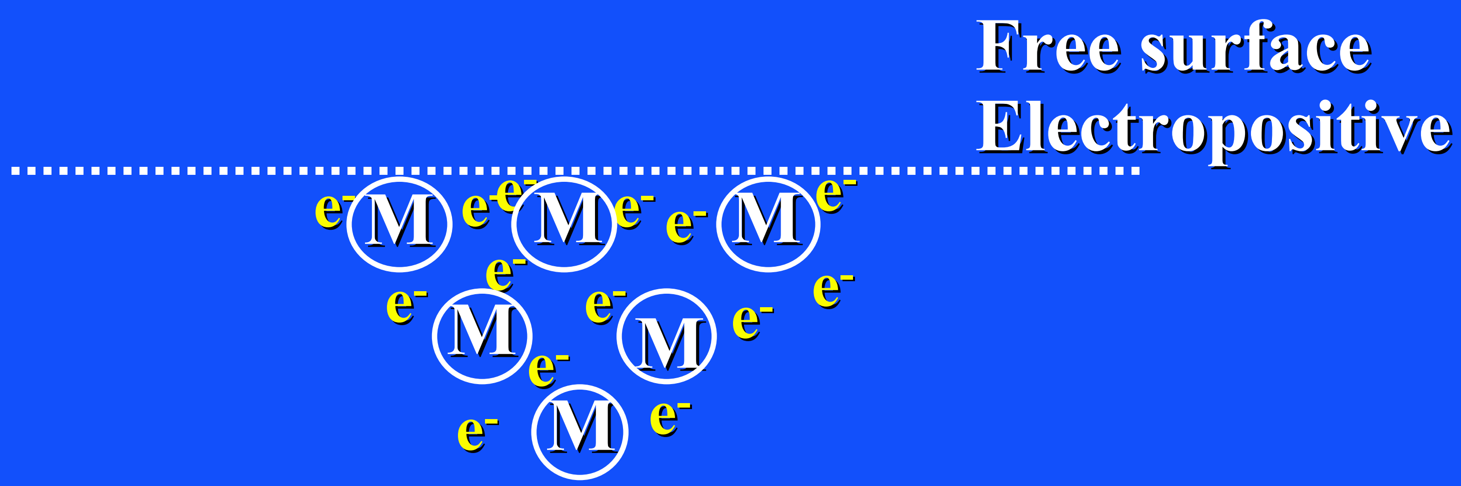
COMPOSITION OF METALS (%)

Stainless Steel	Cobalt Chromium	Titanium
Fe	Co	Ti
Cr (17-20%)	Cr (27-30)	Al (5.5-6.5)
Ni (10-17)	Mo (5-7)	V (3.5-4.5)
Mo (2-4)	Ni (2.5)	Fe,C,O (0.5)
C (0.03)	Fe, C, Mn, Si (<3.1)	
Mn, P, S, Si (<2.8)		

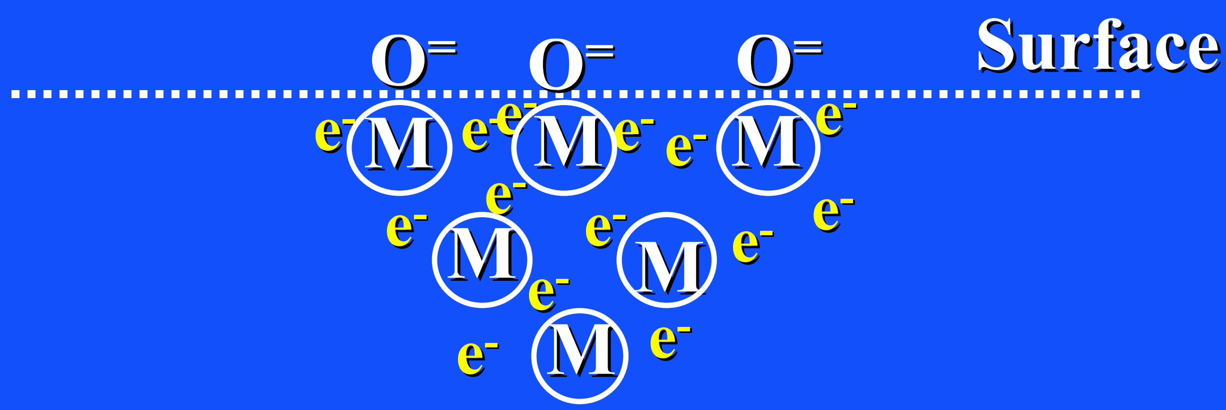
METALS



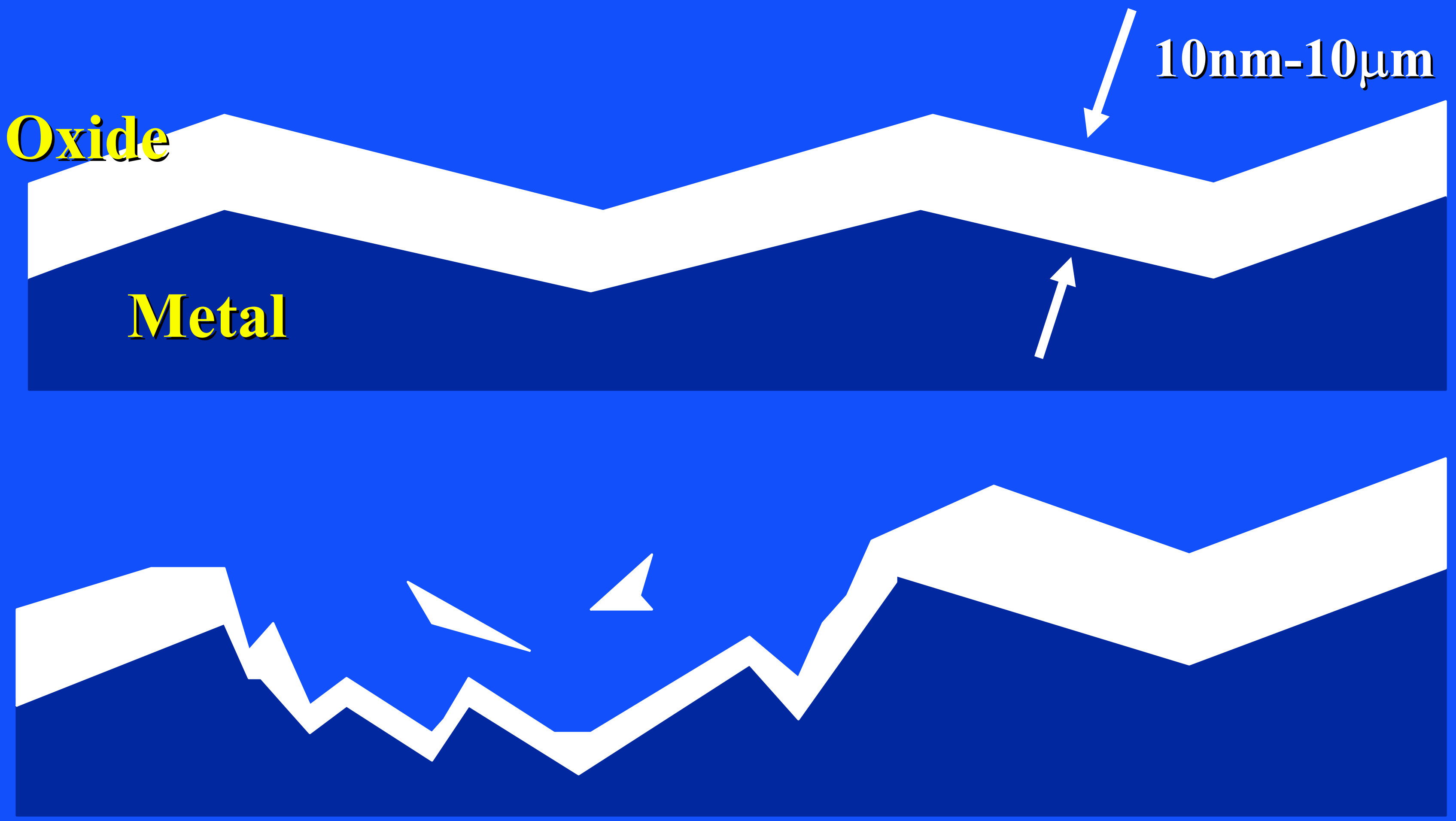
METAL SURFACE



FORMATION OF METALLIC OXIDE



THE METALLIC OXIDE (CERAMIC) SURFACE OF METALS



ORTHOPAEDIC METALS

	ADVANTAGES	DISADVANTAGES
Stainless Steel	Strength Ease of manuf. Availability	Potential for corrosion High mod. of elasticity
Cobalt-Chromium	Strength Rel. wear resist.	High mod. of elasticity
Titanium	Strength Low modulus Corrosion resist.	Poor wear resistance

METALS FOR TJA:
PAST, PRESENT, AND FUTURE

1900-1940	1940-1960	1970	1980	1990	2000	2010

|—— Stainless Steel ——————————

|—— Cobalt-Chromium Alloy ——————

|—— Titanium ——————

|- Oxinium —

Oxinium® (Smith &Nephew Orthopaedics; oxidized zirconium) is the first new metal alloy in orthopaedic surgery in 30 years.

METALS FOR TJA: PAST, PRESENT, AND FUTURE

1900-1940 | 1940-1960 | 1970 | 1980 | 1990 | 2000 | 2010

|—— Stainless Steel ——

|—— Cobalt-Chromium Alloy ——

|—— Titanium ——

|- Oxinium ——

Selection Criteria

|—— Inertness/Biocompatibility ——

|—— Strength ——

|—— Lower Modulus ——

| Scratch-resist.

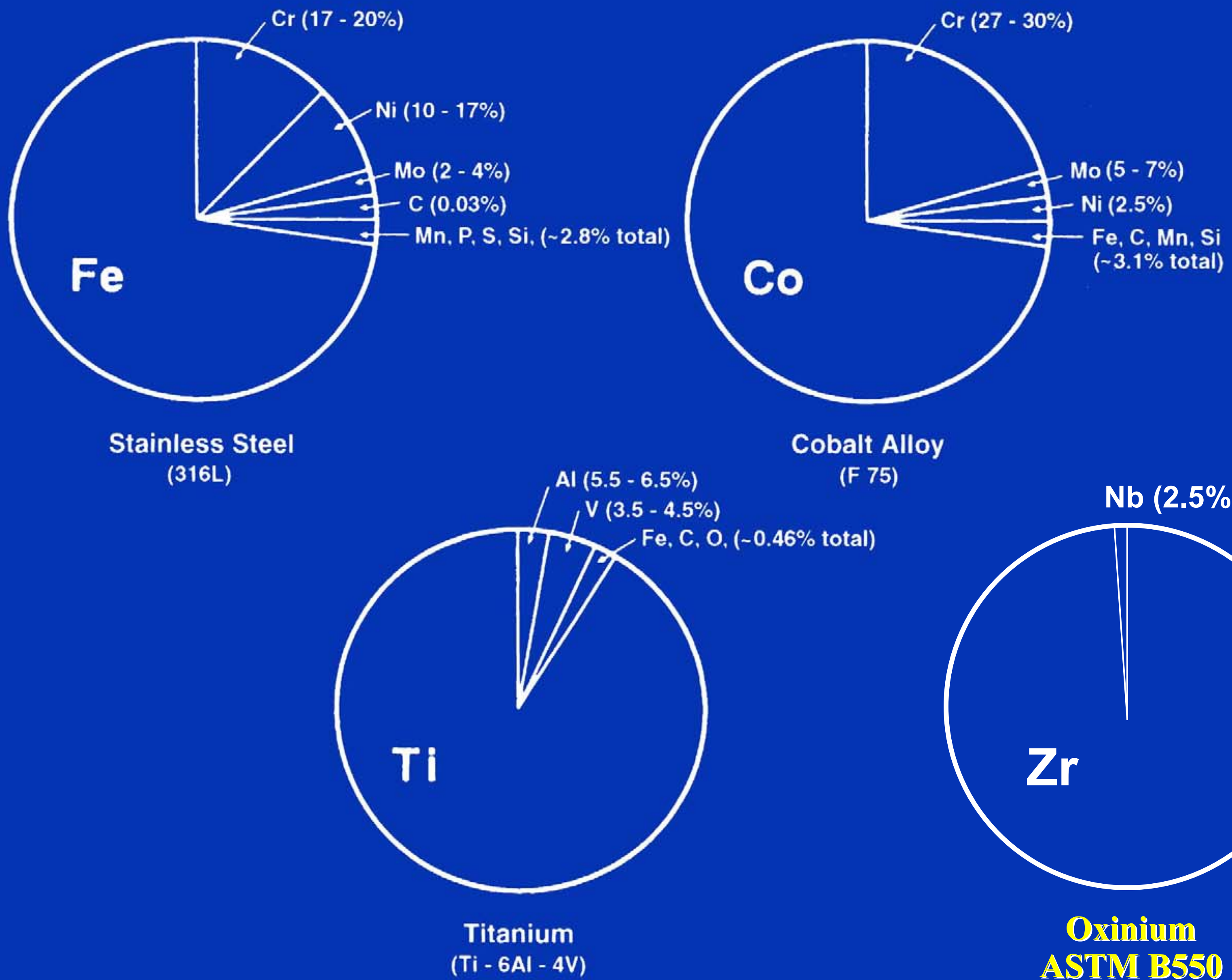
| Lubricatious

| Non-Allergen.

ORTHOPAEDIC METALS

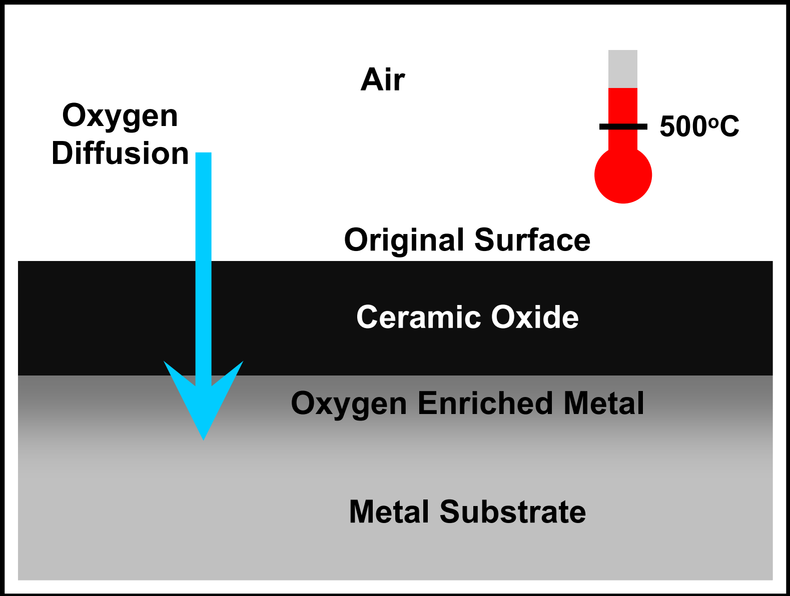
	ADVANTAGES	DISADVANTAGES
Stainless Steel	Strength Ease of manuf. Availability	Potential for corrosion High mod. of elasticity
Cobalt-Chromium	Strength Rel. wear resist.	High mod. of elasticity
Titanium	Strength Low modulus Corrosion resist.	Poor wear resistance
Oxinium	Scratch-resist. Low modulus	?

Composition of Orthopaedic Metals



How is the Ceramic Surface Produced on Oxinium?: Oxidation Process

- Wrought zirconium alloy device is heated in air.
- Metal transforms as oxide grows; not a coating.
- Zirconium Oxide (Zirconia ceramic) is ~5 μm thick.



Zirconium metal alloy is heated in air

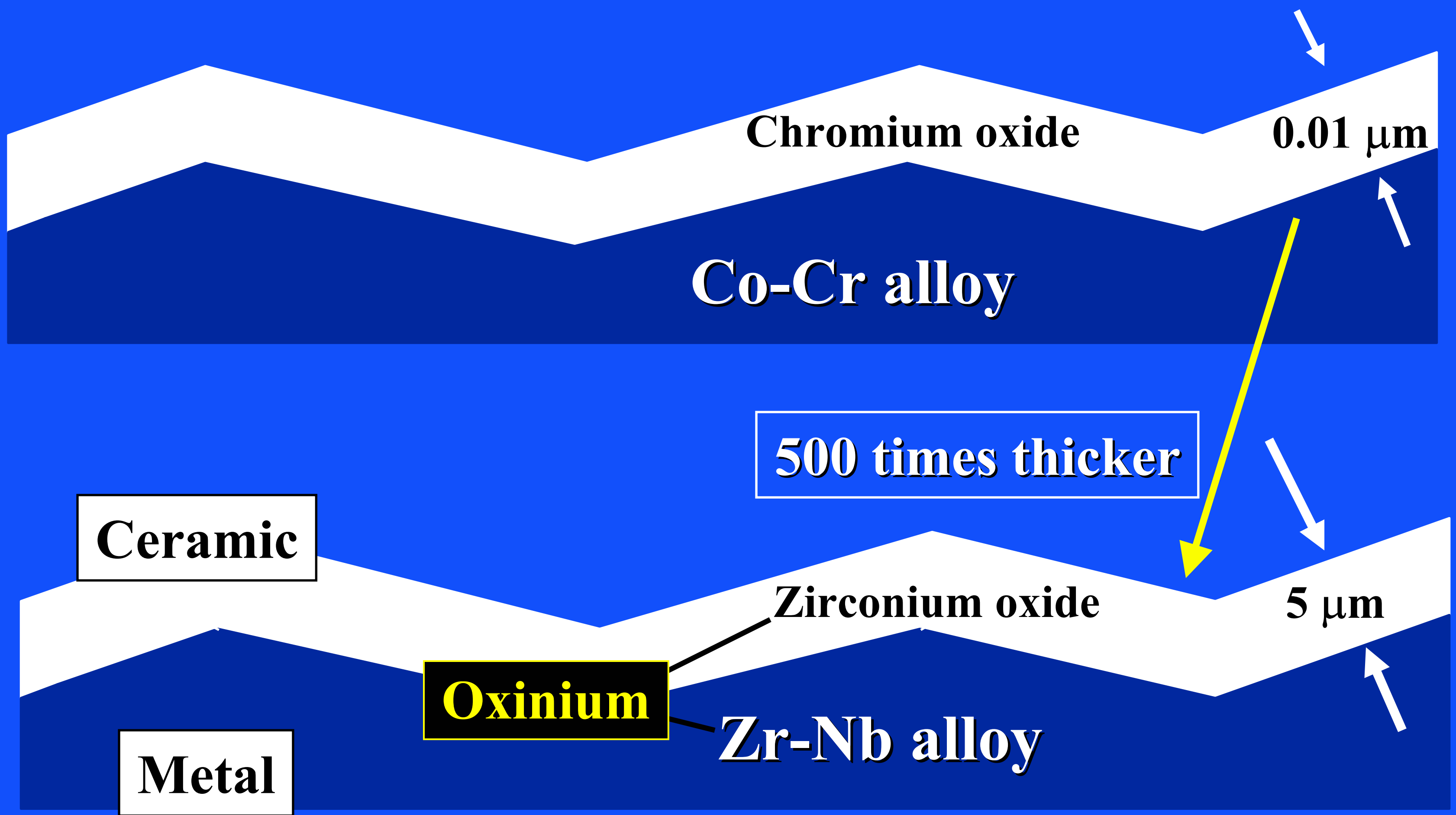
Oxygen diffuses into the metal surface

Surface becomes enriched in oxygen

Surface transforms to ceramic oxide

G. Hunter, S&N

Co-Cr ALLOY VERSUS Zr-Nb ALLOY: THICKNESS OF THE OXIDE



Fatigue Testing of Oxinium Femoral Components

- Fatigue strength the same as for Co-Cr devices.
- Supports 4.4 kN (1000 lbf) in 10 Mcycle fatigue test.
- Tested worst-case: thin condyle, no bone, full flexion.

Image removed due to copyright considerations.

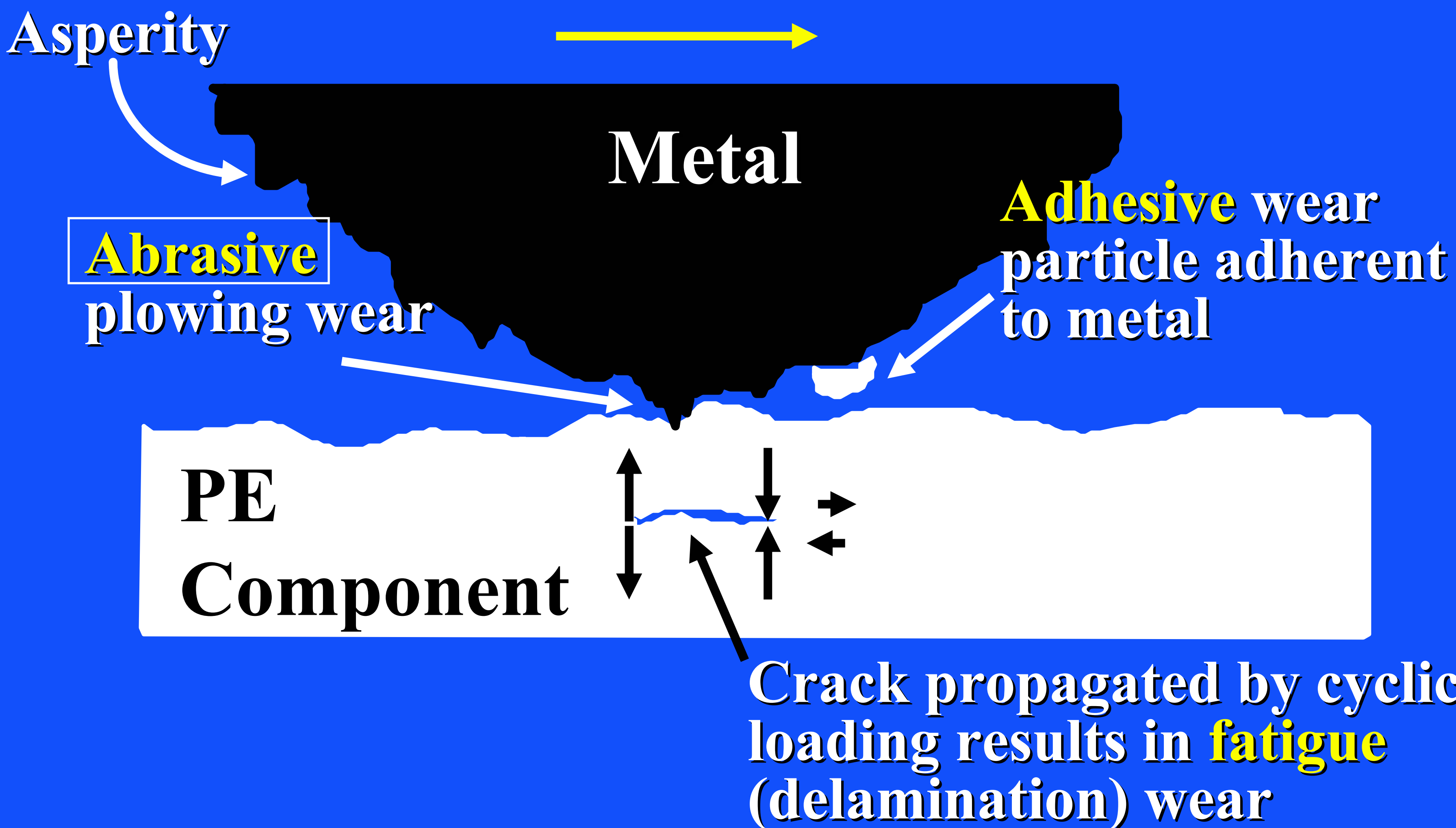
*Tsai et al., SFB 2001

ADVANTAGES OF OXINIUM

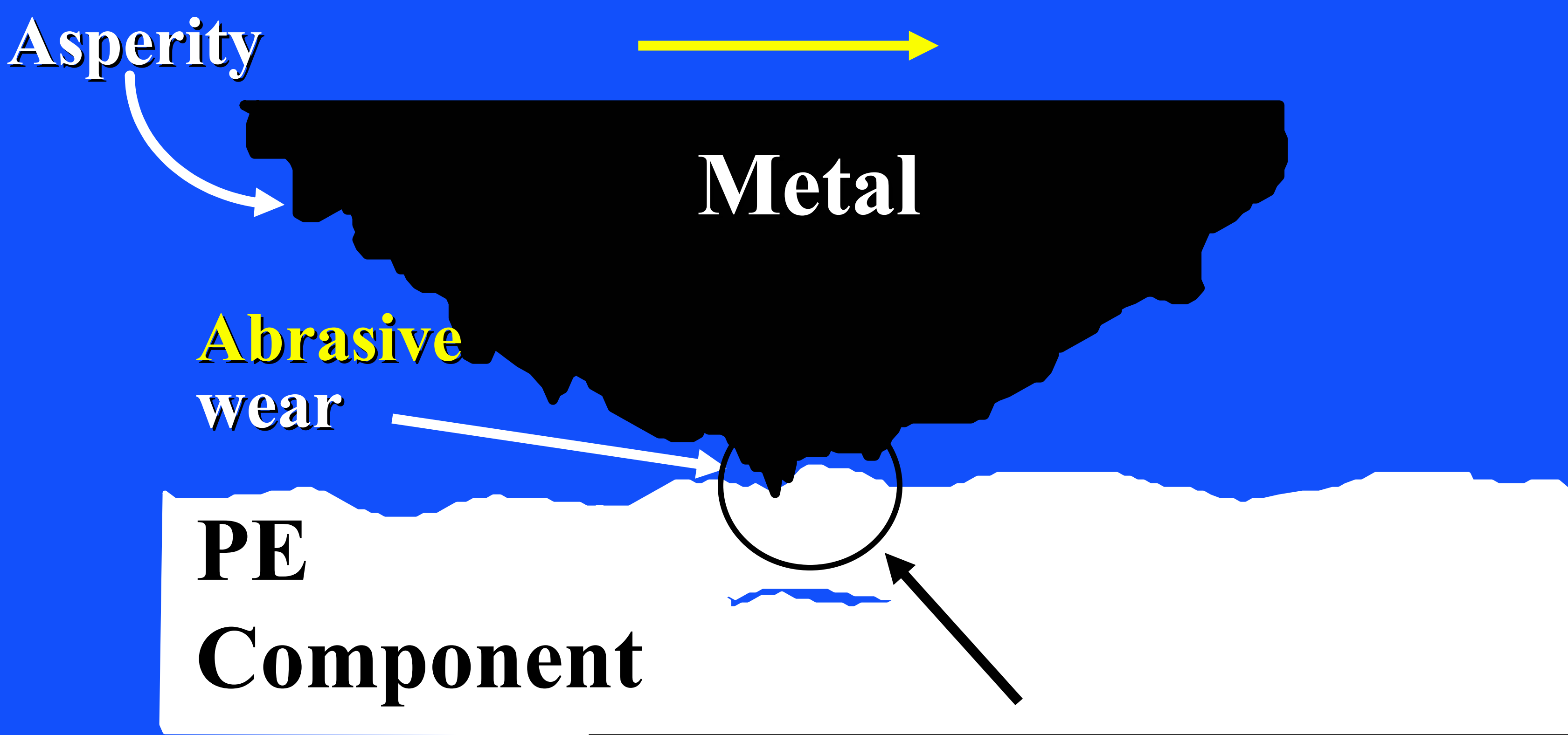
Weds the best of a ceramic with the best of a metal.

- Scratch resistant: less abrasive wear of PE
- More lubricatious: lower friction may result in less adhesive wear of PE; better patella articulation
- Much lower modulus than Co-Cr alloy (similar to Ti): lower stiffness and less stress shielding
- Non-allergenic

WEAR PROCESSES



WEAR PROCESSES



Solution is a scratch-resistant metal/ceramic counterface; X-linked PE may not be the solution

EFFECT OF A SINGLE SCRATCH ON PE WEAR

- **Profound effect of a single scratch; wear due to the ridge of metal bordering an scratch**

10-fold increase in PE wear when the ridge bordering the scratch exceeded 2μm in height

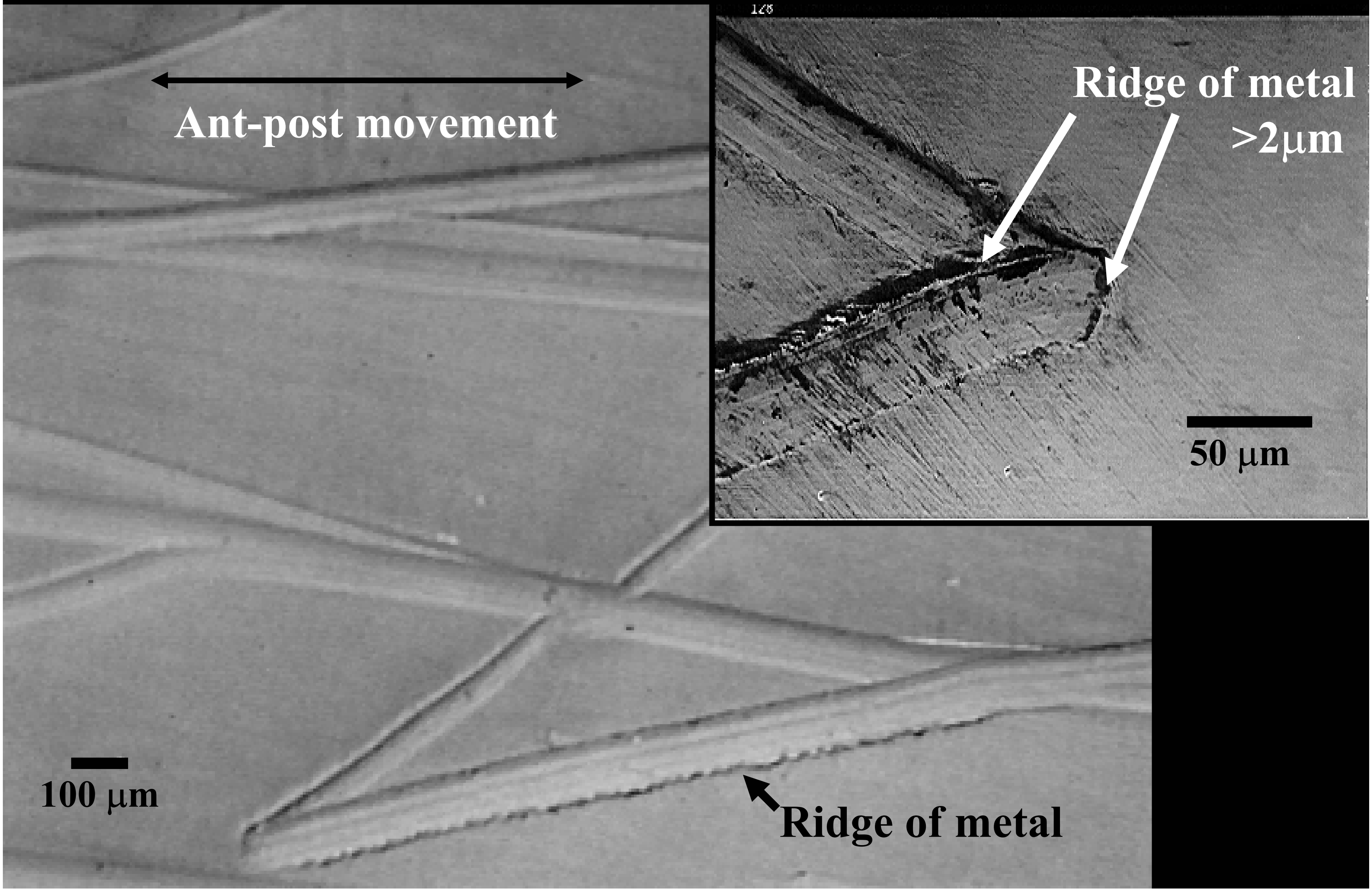
Image removed due to copyright considerations.

No PE wear if the metal ridge is removed

(This type of scratch is not noticeable by eye.)

Dowson, *et al.*, Wear (1987)

Scratches on Retrieved Co-Cr Femoral Condyles
Scanning Electron Microscopy



SOURCES OF PARTICLES THAT CAUSE SCRATCHES ON CONDYLES

- **Bone**
- **PMMA (bone cement)**
- **Wear and corrosion products from modular junctions**
- **Prosthetic coatings (*viz.*, plasma sprayed Ti)**

Is ceramic-on-PE the answer ?

Alumina or zirconia heads

Image removed due to copyright considerations.

IF CERAMIC IS THE ANSWER

How to obtain the benefit of ceramic-on-PE articulation in TKA? Bulk ceramics do not have the necessary mechanical properties for TKA.

Answer:

A new metal alloy, zirconium niobium (Oxinium), the surface of which can be oxidized to form zirconium oxide (zirconia), a durable scratch-resistant ceramic.

Oxinium

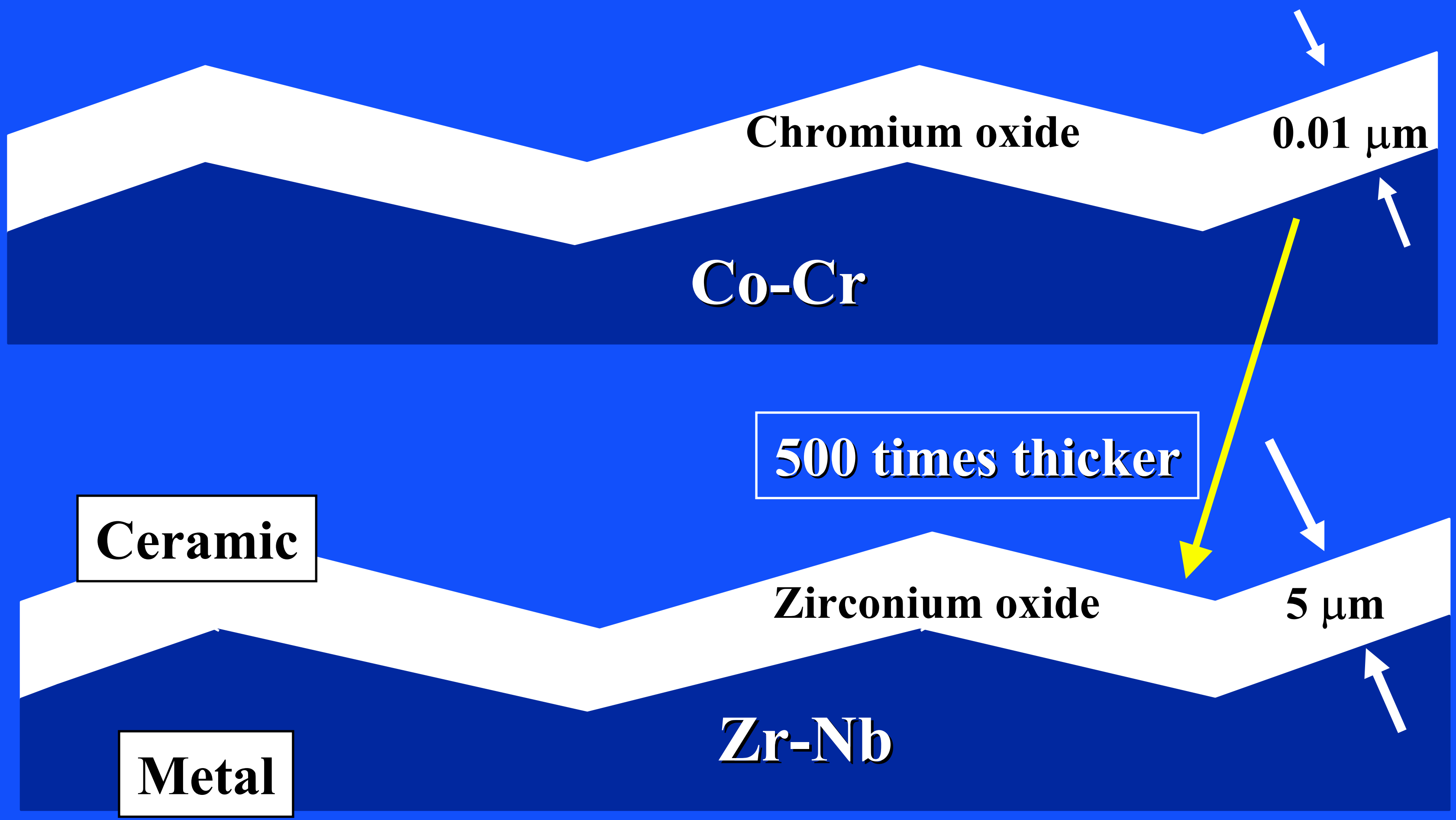
Image removed due to copyright considerations.

- **May be a more innovative a development than cross-linked PE.**
- **One of only 2 materials developed principally for TJA (the other is hydroxyapatite).**

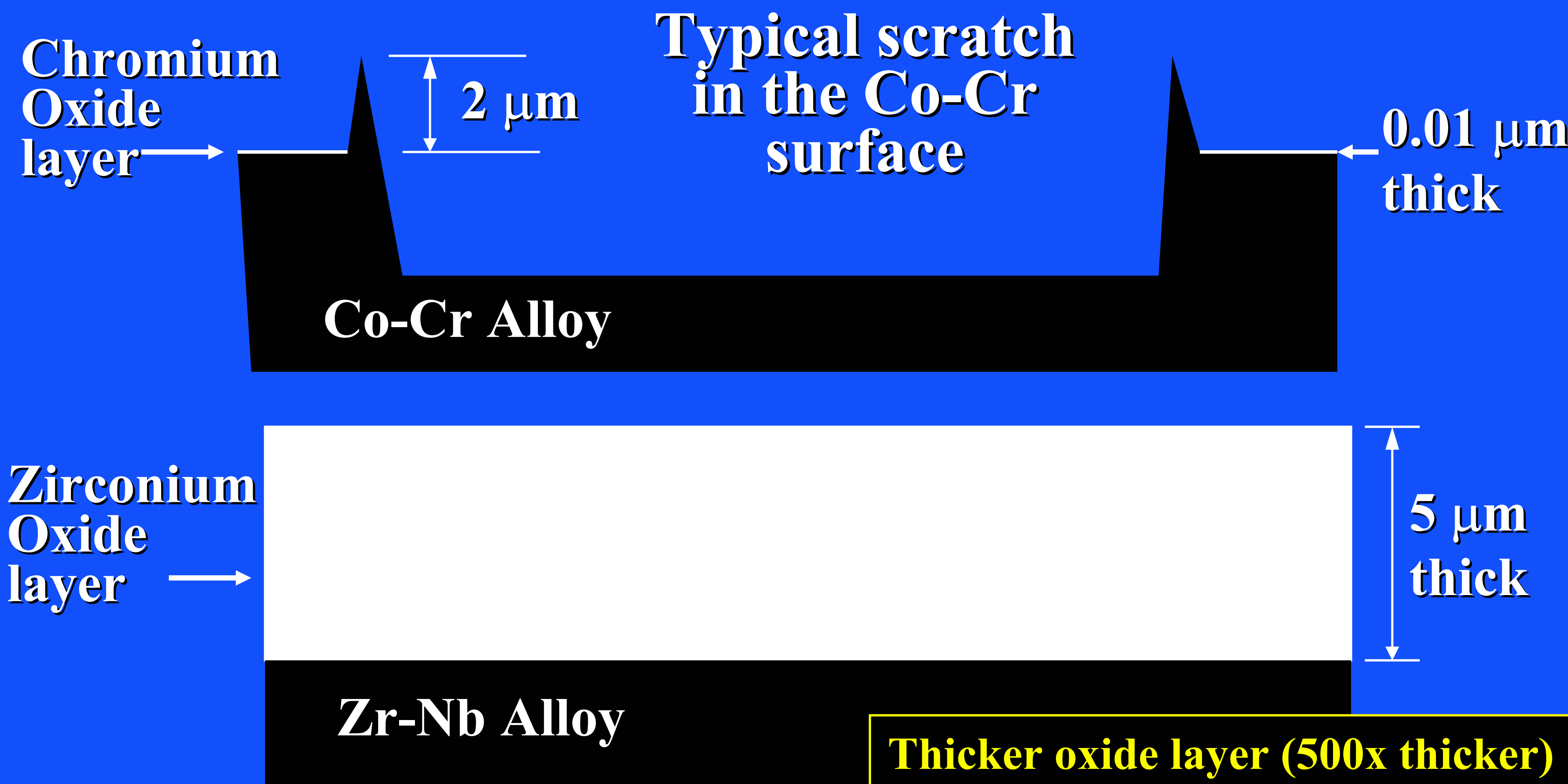
CHARACTERISTICS OF OXIDES THAT AFFECT THEIR PERFORMANCE

- Thickness
- Adherence to metal substrate
- Porosity/density/strength of the oxide

Co-Cr ALLOY VERSUS Zr-Nb ALLOY THICKNESS OF THE OXIDE



COMPARISON OF THE OXIDE THICKNESSES ON Co-Cr AND Zr-Nb



Thicker oxide layer (500x thicker) to protect against scratches.

ADHERENCE OF Zr OXIDE TO THE METAL

Transmission Electron Microscopy

Interface between oxide and metal:

-no voids

-no imperfections

Prof. L.W. Hobbs, MIT

Zirconium oxide

Image removed due to copyright considerations.

ZrO_2 thickness

Cr_2O_3

Zirconium metal

V Benezra, *et al.*
MRS Symp., 1999

STRENGTH OF Zr OXIDE

Transmission Electron Microscopy

Zirconium oxide

Rectangular crystals of $Zr0_2$

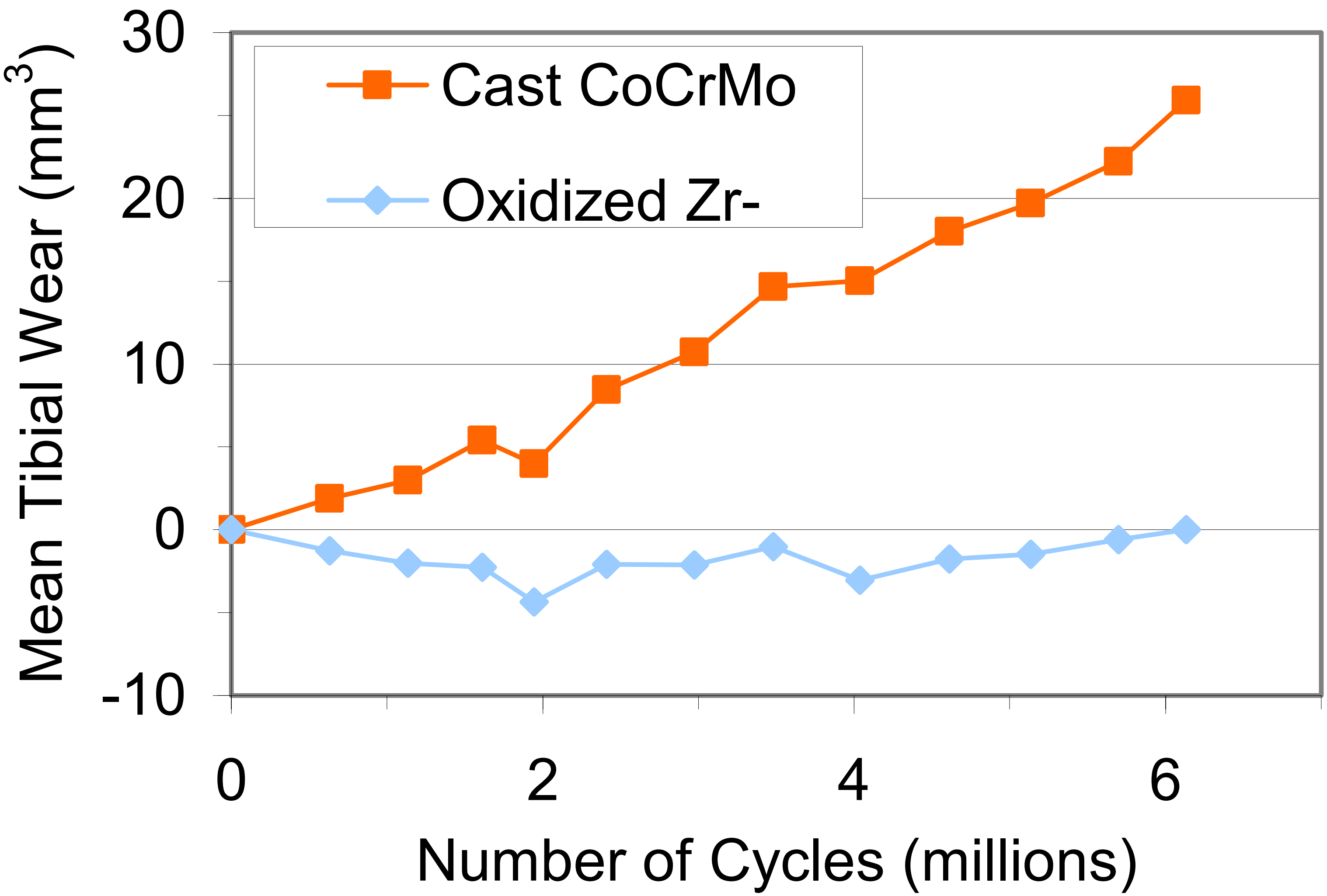
"Brick Wall Tough"

Image removed due to copyright considerations.

Zirconium metal

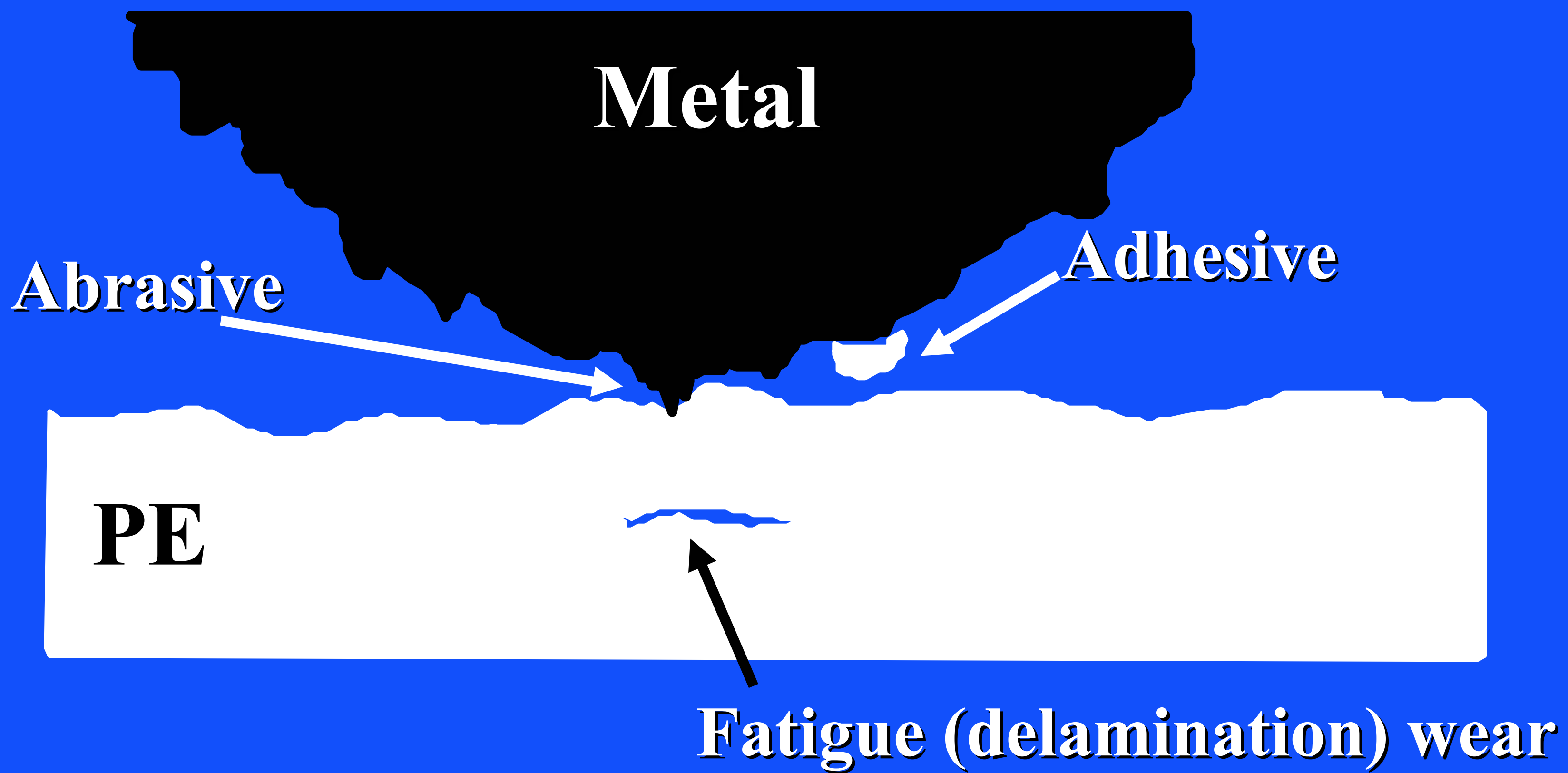
V Benezra, *et al.* MRS Symp., 1999

Wear of PE with OxZr versus CoCr Condyles
Knee Simulator Study



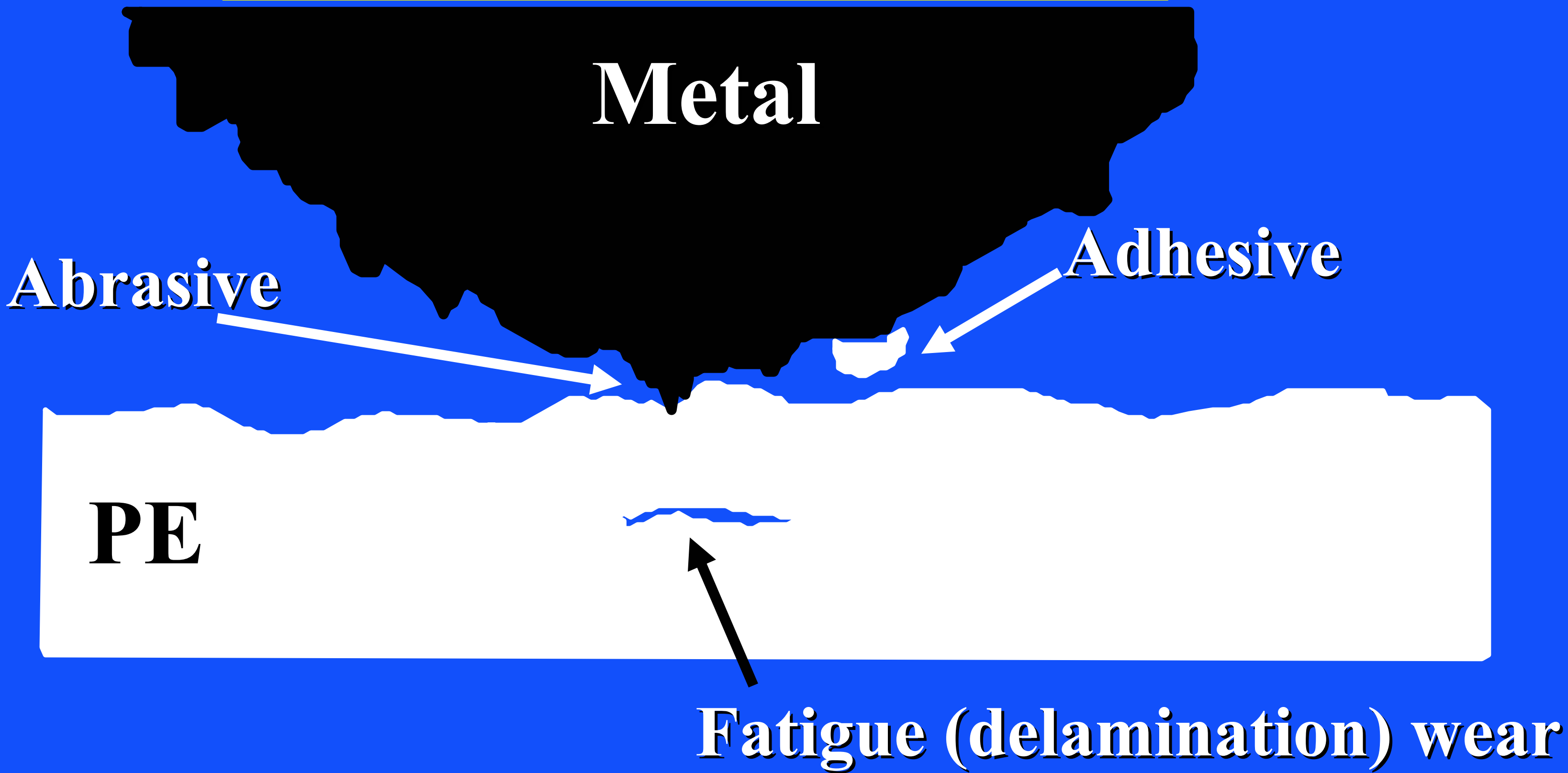
Smith & Nephew Orthopaedics

WEAR PROCESSES
Materials Issues

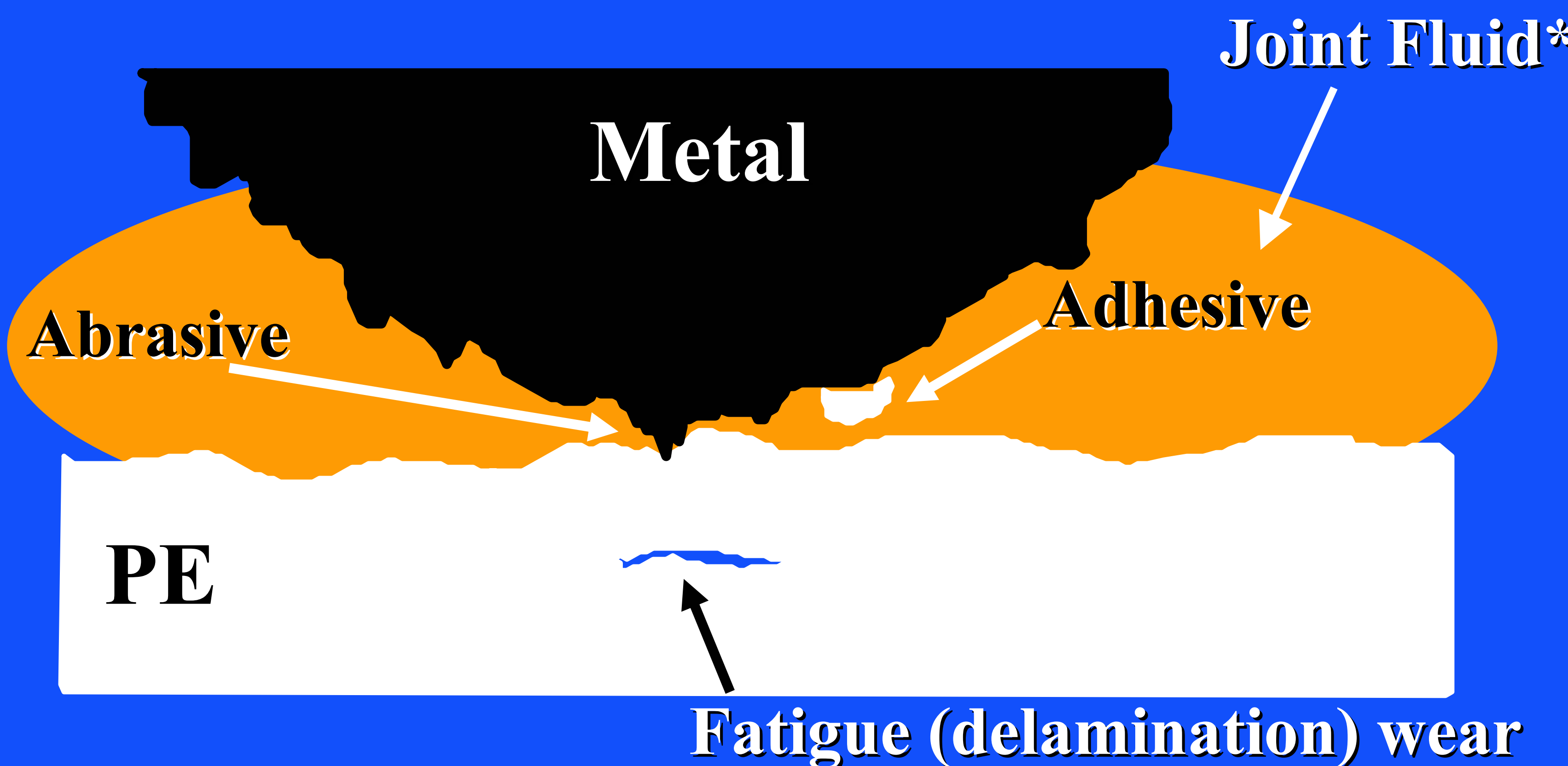


WEAR PROCESSES
Materials Issues

What is missing from this picture?



WEAR PROCESSES
Materials Issues



* What role does the joint fluid play in the tribology of TJA?

WEAR IN TOTAL JOINT ARTHROPLASTY

Tribology

- Lubrication
  - Depends on amount, composition and mechanical properties of joint fluid
- Friction
  - Better the lubrication lower the friction
- Wear
  - Lower the friction, less wear

Wear testing of a total knee replacement prostheses in a "knee simulator."

Image removed due to copyright considerations.

Bovine serum; <u>not</u> water

Image removed due to copyright considerations.

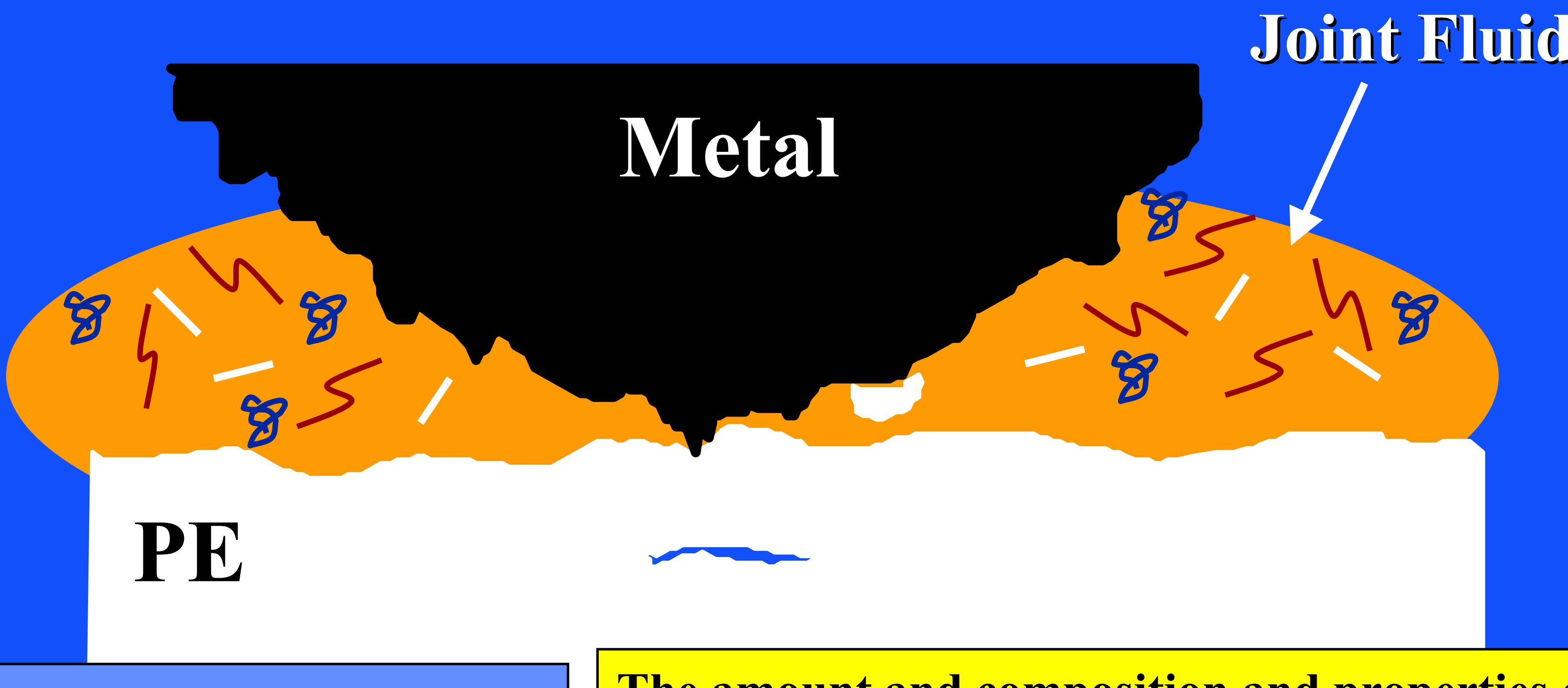
How good a lubricant is the patient's joint fluid?

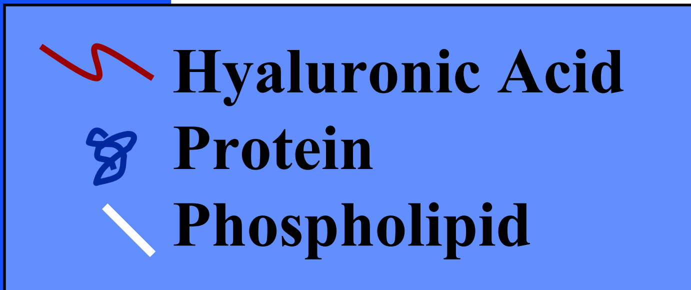
COMPOSITION AND MECHANICAL PROPERTIES OF JOINT FLUID IN PRIMARY AND REVISION TKA

- Differences in certain compositional features and certain mechanical properties of joint fluid from revision cases when compared to the properties of fluid from patients before TKA.
- How well can joint fluid lubricate TKA?

D. Mazzucco and M. Spector, J. Orthop. Res. 2002;20:1157-1163
D. Mazzucco, et al., Biomat., (In press)

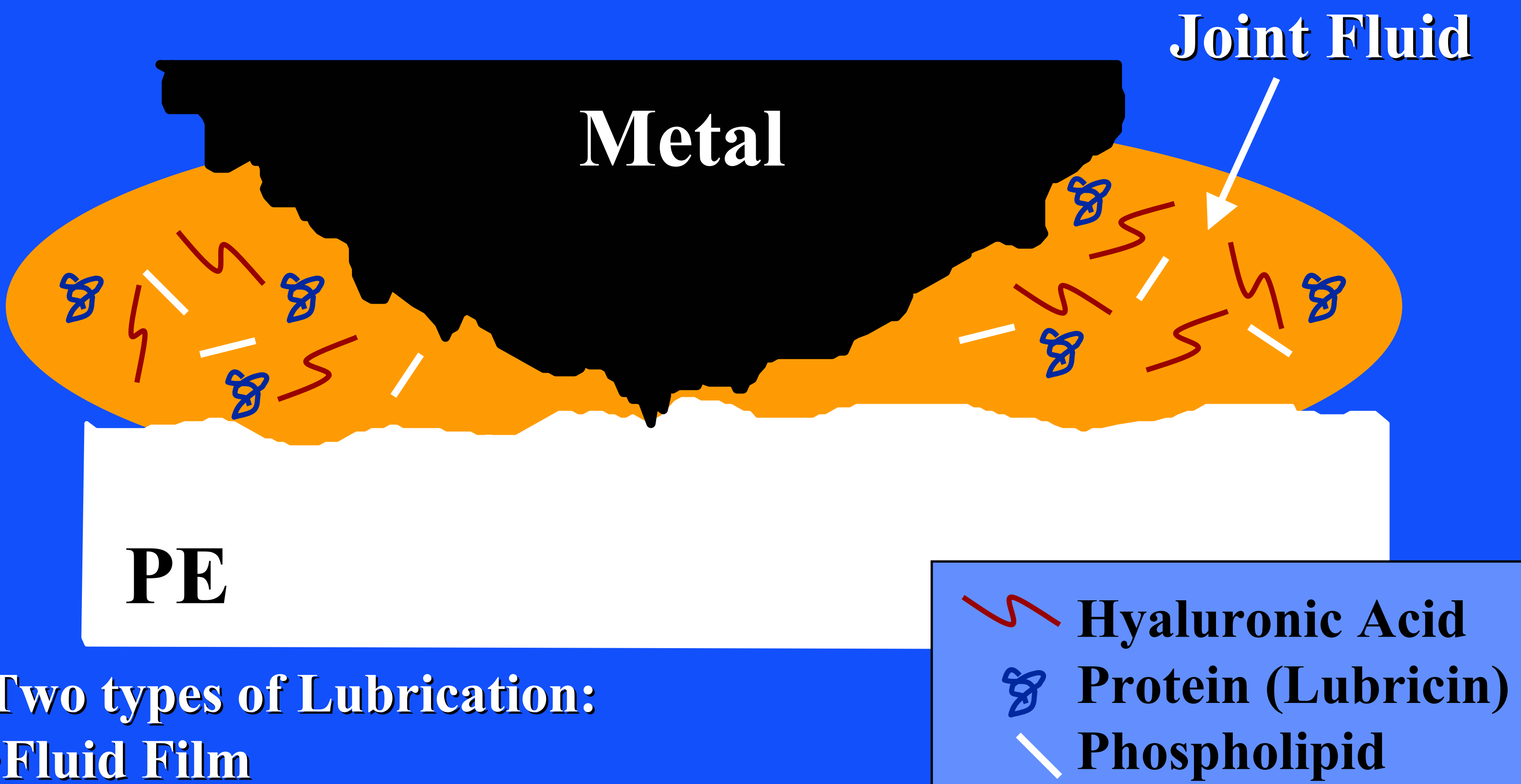
COMPOSITION OF JOINT FLUID





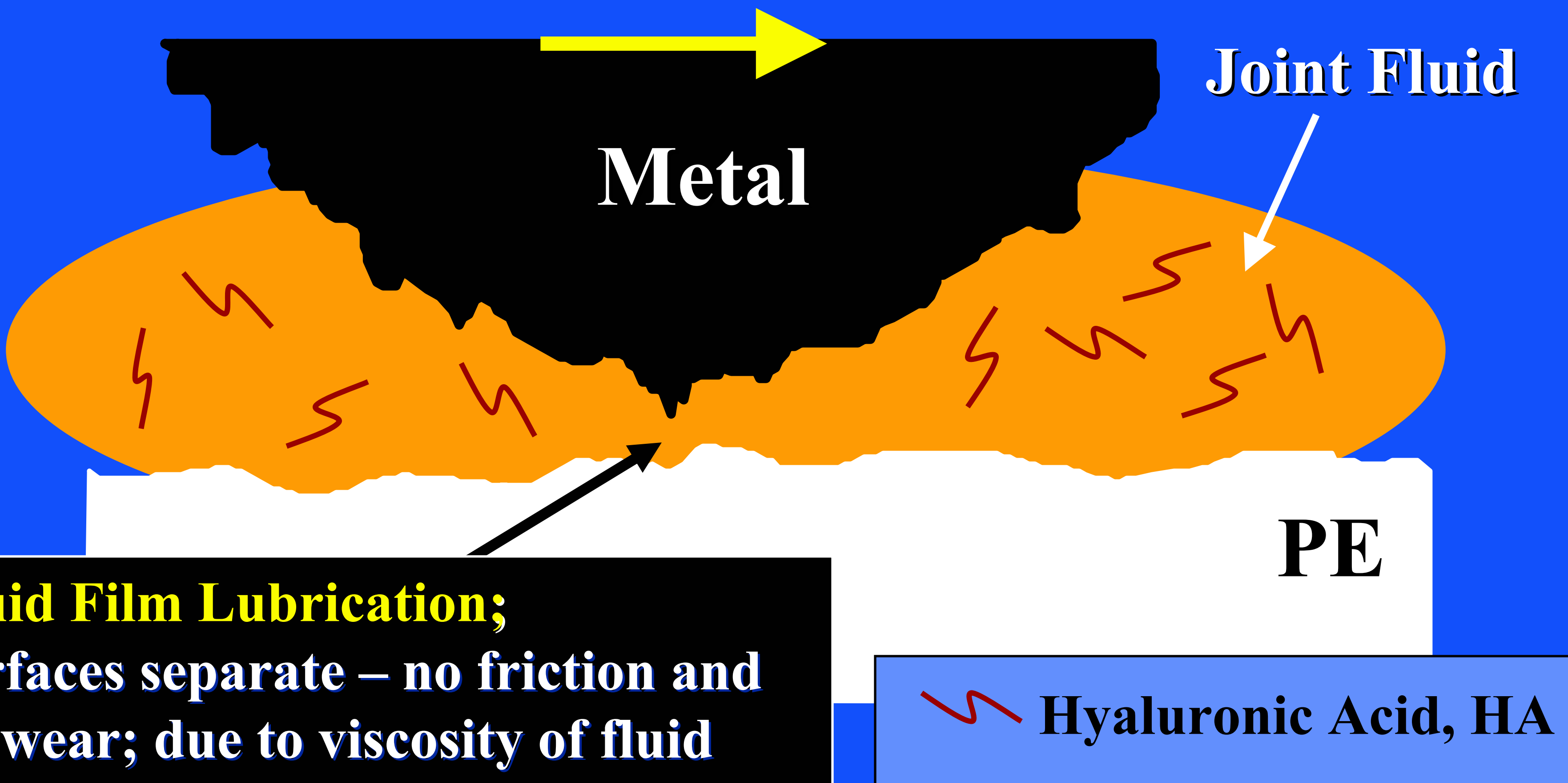
The amount and composition and properties of joint fluid in TKA patients vary widely; this could explain why some pts. have high wear. Solution; Metal with lower friction even in presence of abnormal joint fluid.

COMPOSITION OF JOINT FLUID



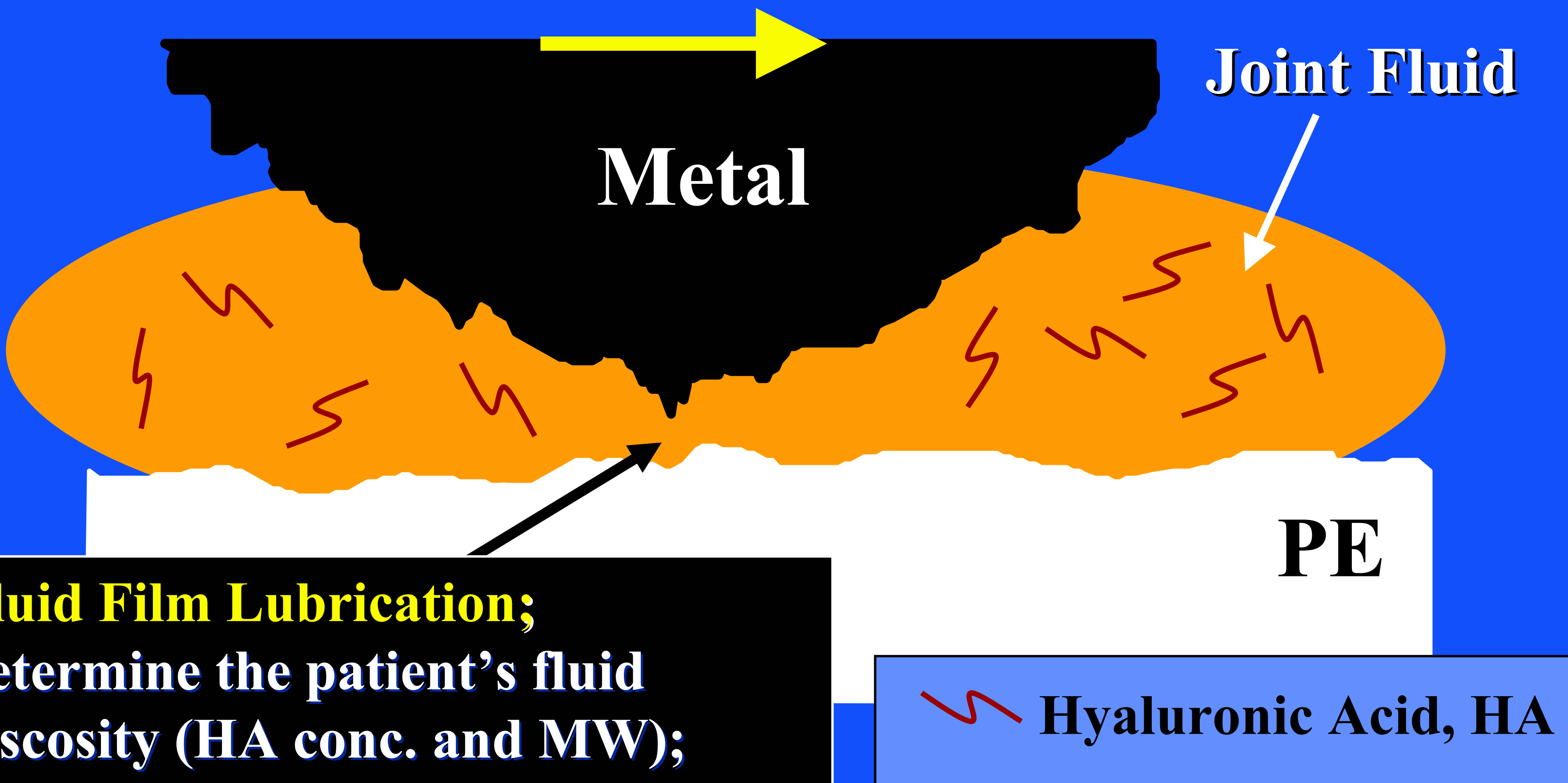
Two types of Lubrication:
- Fluid Film
- Boundary Layer

WEAR PROCESSES
Fluid Film Lubrication



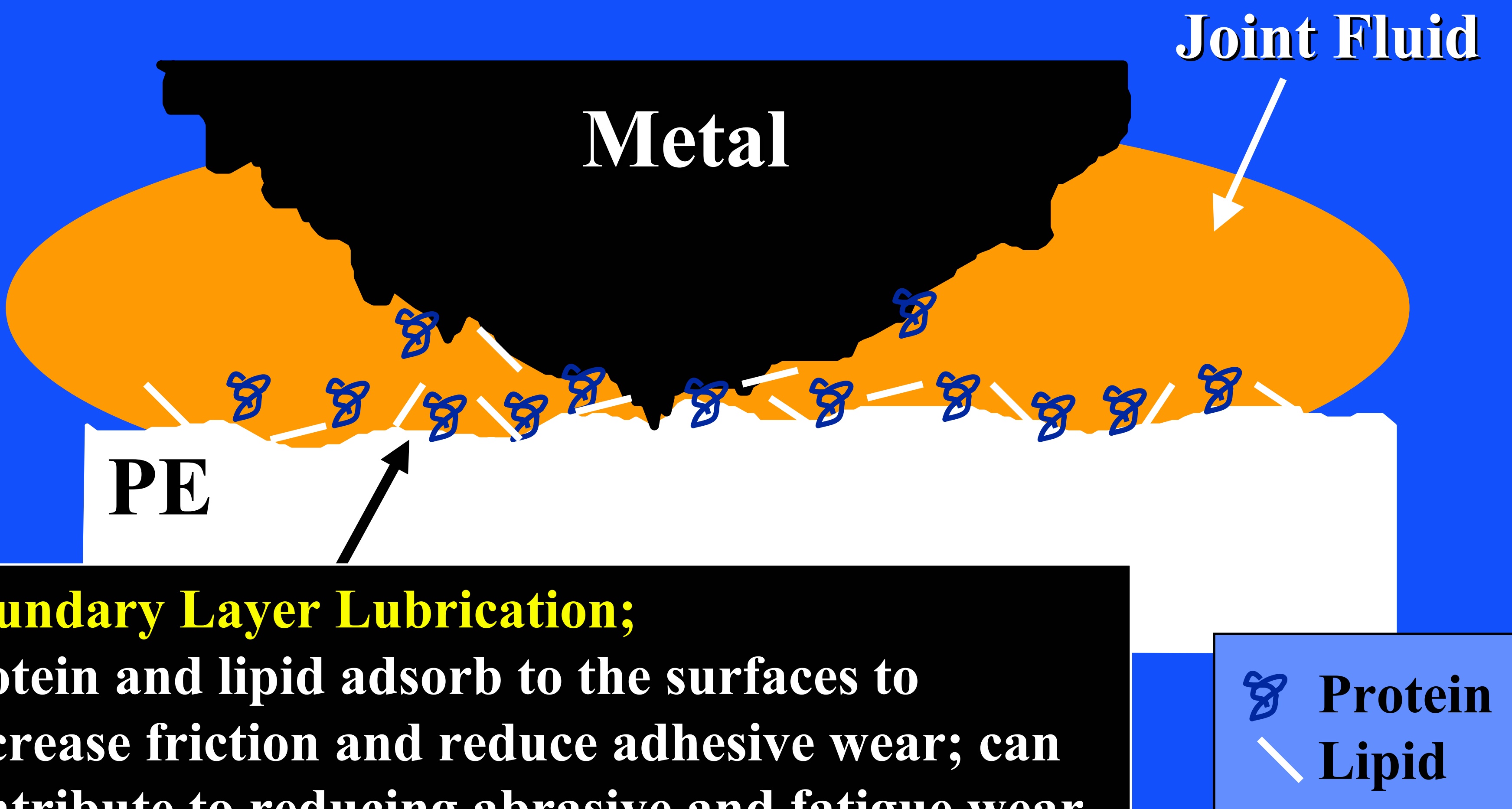
Fluid Film Lubrication;
surfaces separate – no friction and no wear; due to viscosity of fluid (HA conc. and MW), topography of counterfaces, and velocity: TKA?

WEAR PROCESSES
Fluid Film Lubrication



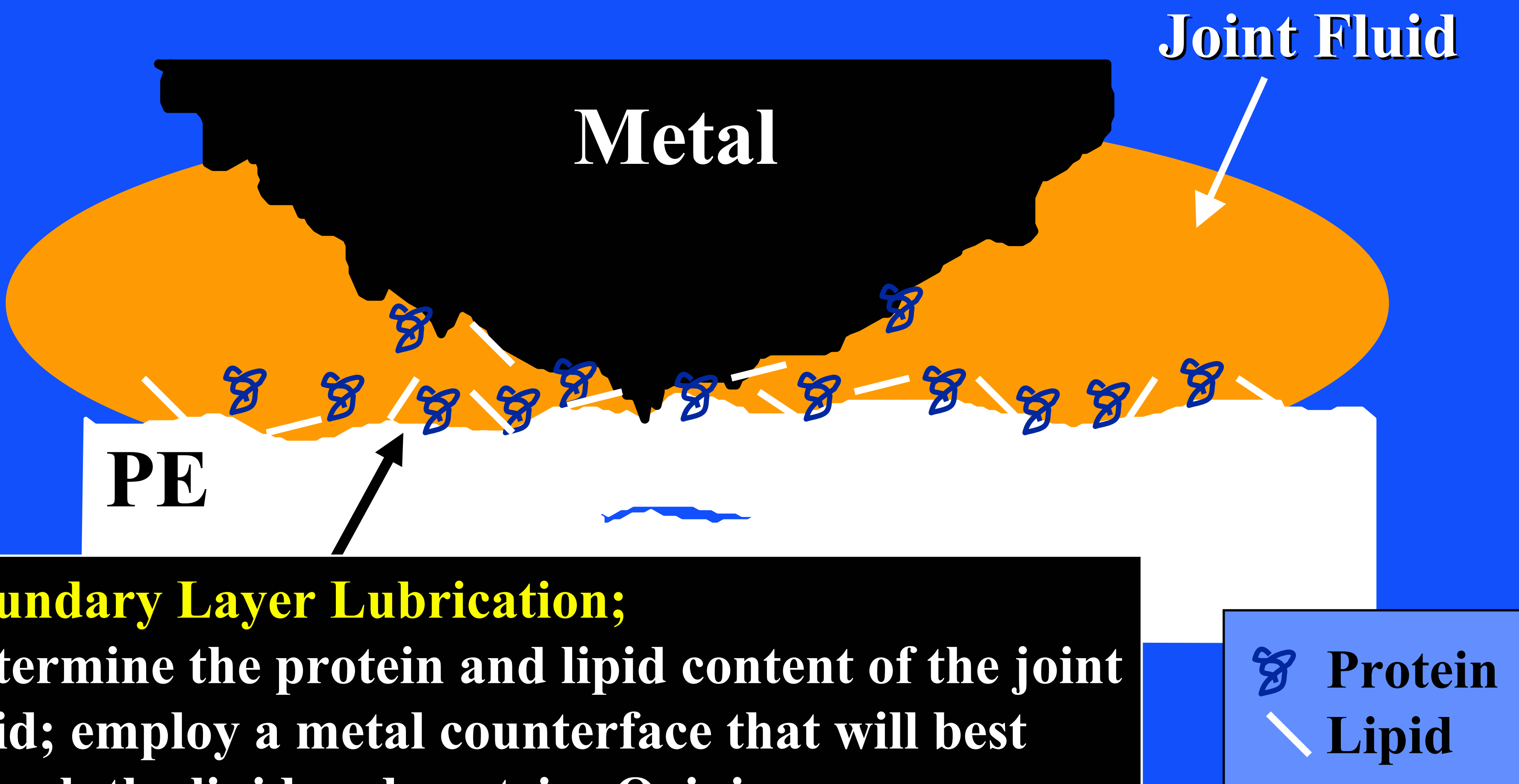
Fluid Film Lubrication;
determine the patient's fluid viscosity (HA conc. and MW); benefit of HA injection?

WEAR PROCESSES
Boundary Layer Lubrication



Boundary Layer Lubrication;
protein and lipid adsorb to the surfaces to decrease friction and reduce adhesive wear; can contribute to reducing abrasive and fatigue wear

WEAR PROCESSES
Boundary Layer Lubrication



Boundary Layer Lubrication;
Determine the protein and lipid content of the joint fluid; employ a metal counterface that will best adsorb the lipid and protein; Oxinium

ADVANTAGES OF OXINIUM

Weds the best of a ceramic with the best of a metal.

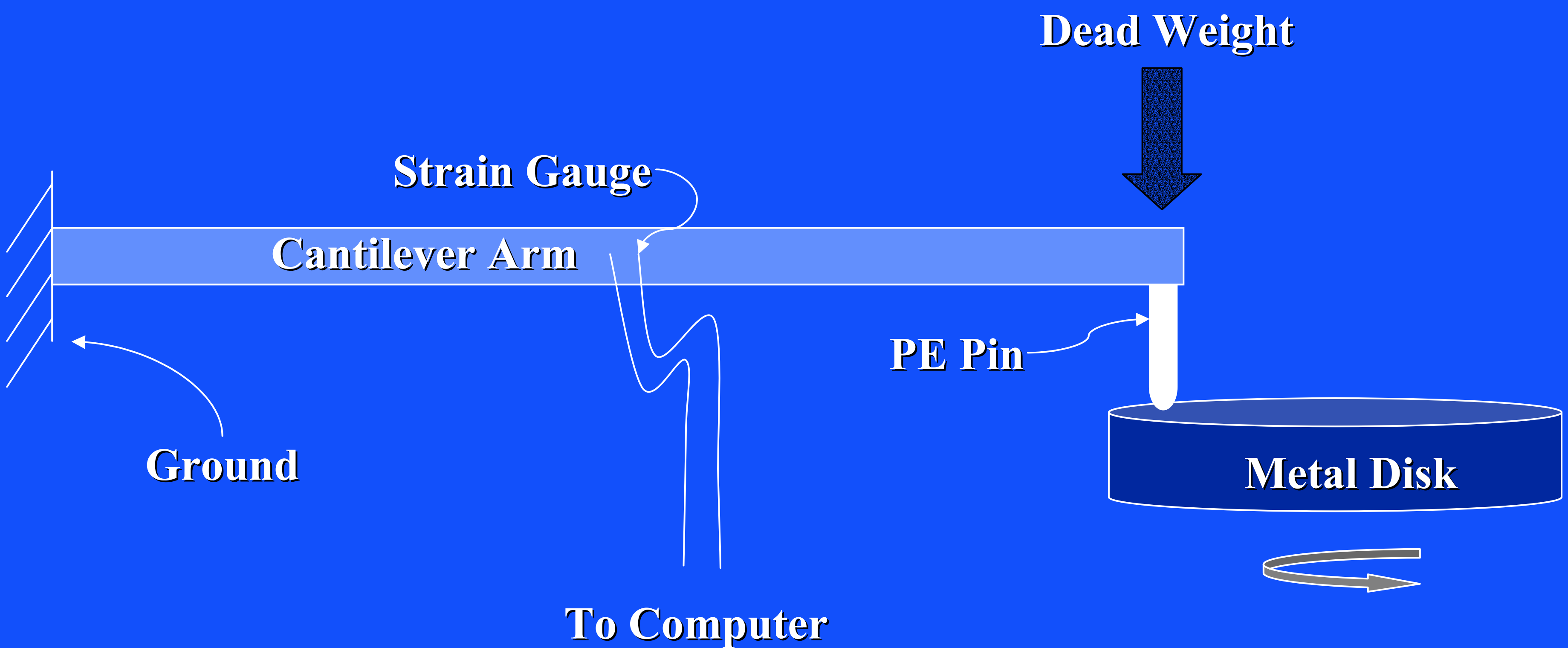
- **Scratch resistant: less abrasive wear of PE**
- **Better lubricity than Co-Cr alloy: lower friction may result in less adhesive wear of PE; better patella articulation**
- **Much lower modulus than Co-Cr alloy (similar to Ti): lower stiffness and less stress shielding**
- **Non-allergenic**

WEAR IN TOTAL JOINT ARTHROPLASTY

Tribology

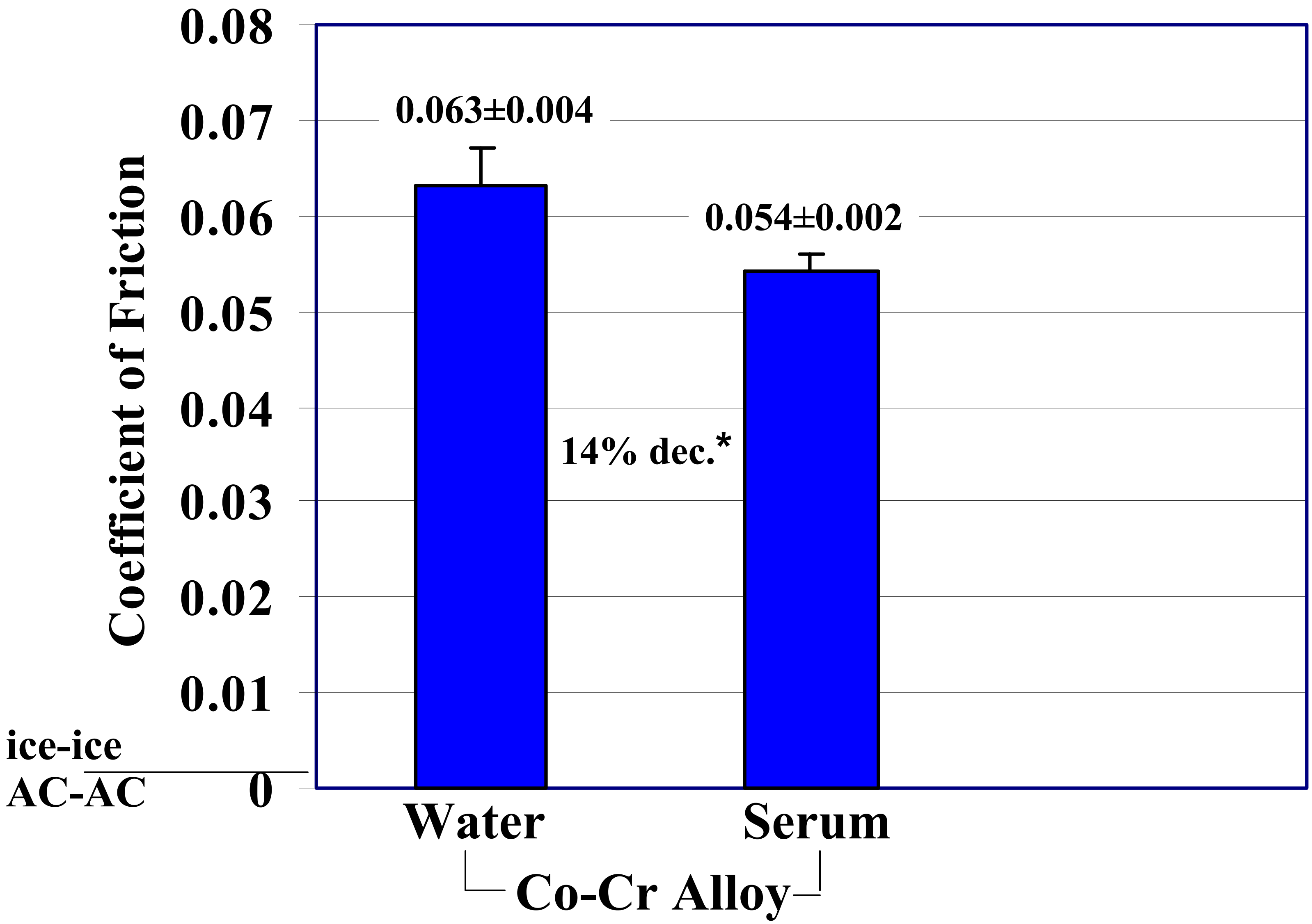
- Lubrication
  - Depends on amount, composition and mechanical properties of joint fluid
- Friction
  - Better the lubrication lower the friction
- Wear
  - Lower the friction, less wear

FRICTION APPARATUS



Coef. of friction (μ)=lateral force/normal force

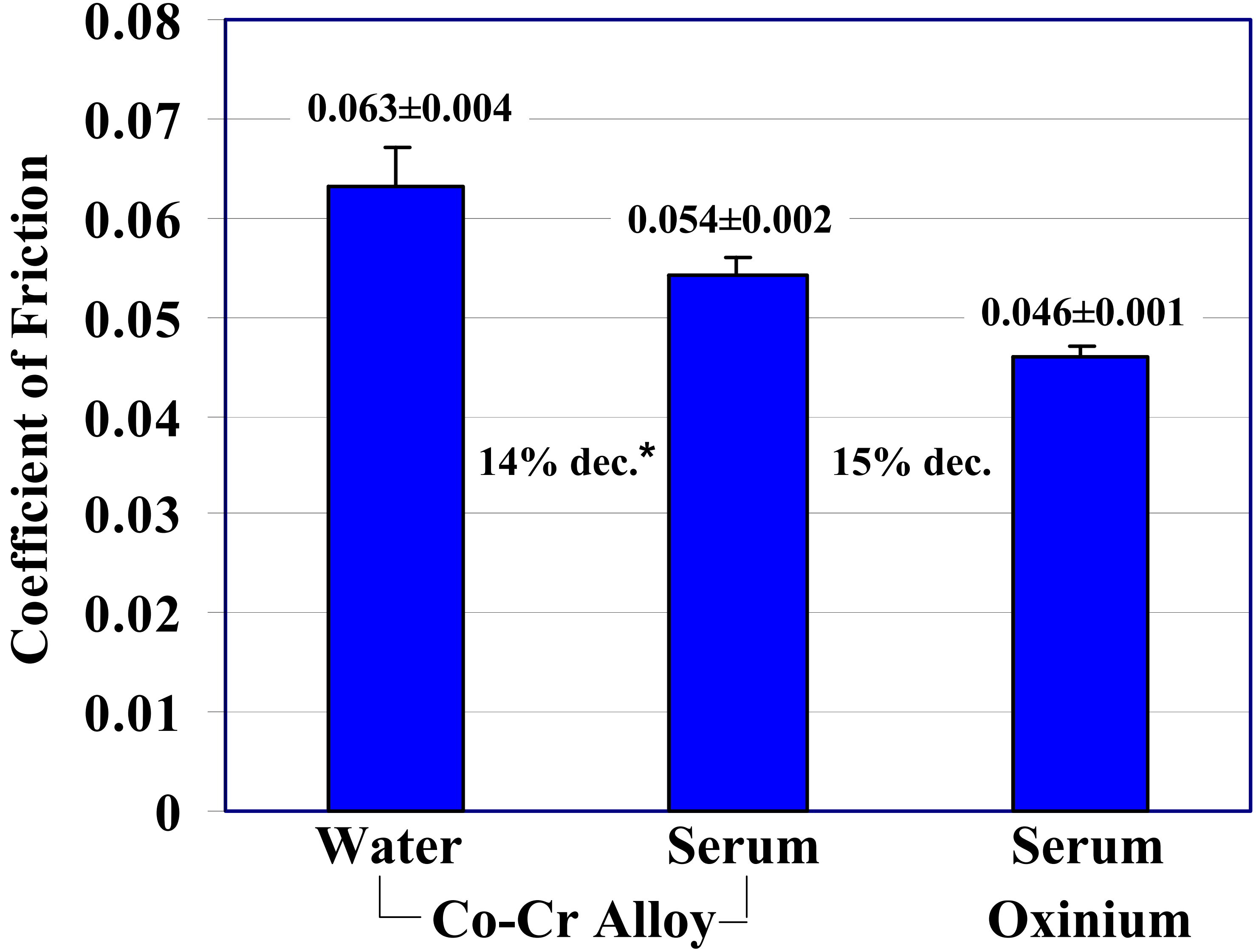
Friction of Oxinium with PE versus Co-Cr



* Wear of PE in serum< $^{1}/_{3}$ wear in water

Mazzucco & Spector

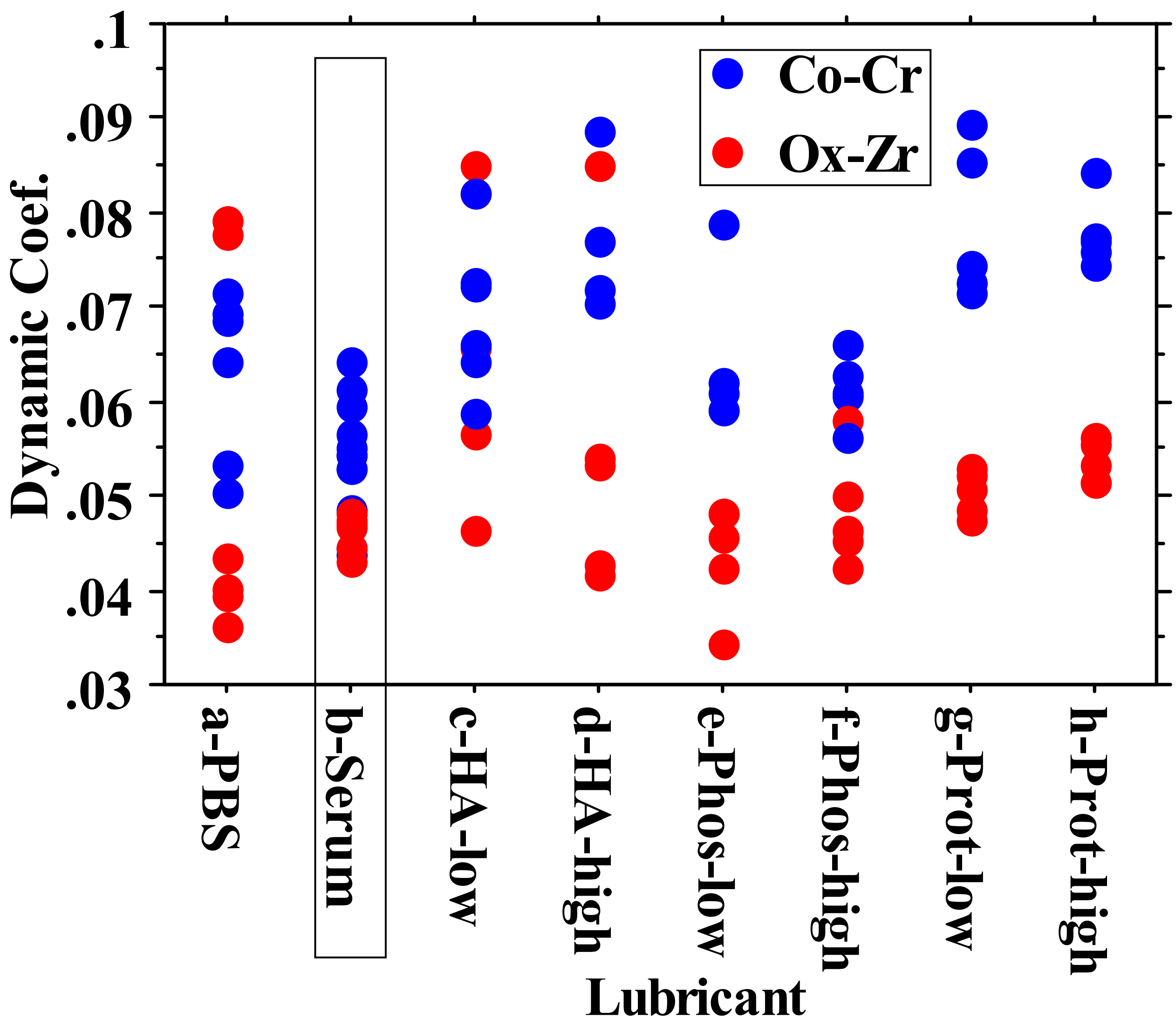
Friction of Oxinium with PE versus Co-Cr



* Wear of PE in serum<$^{1}/_{3}$ wear in water

Mazzucco & Spector

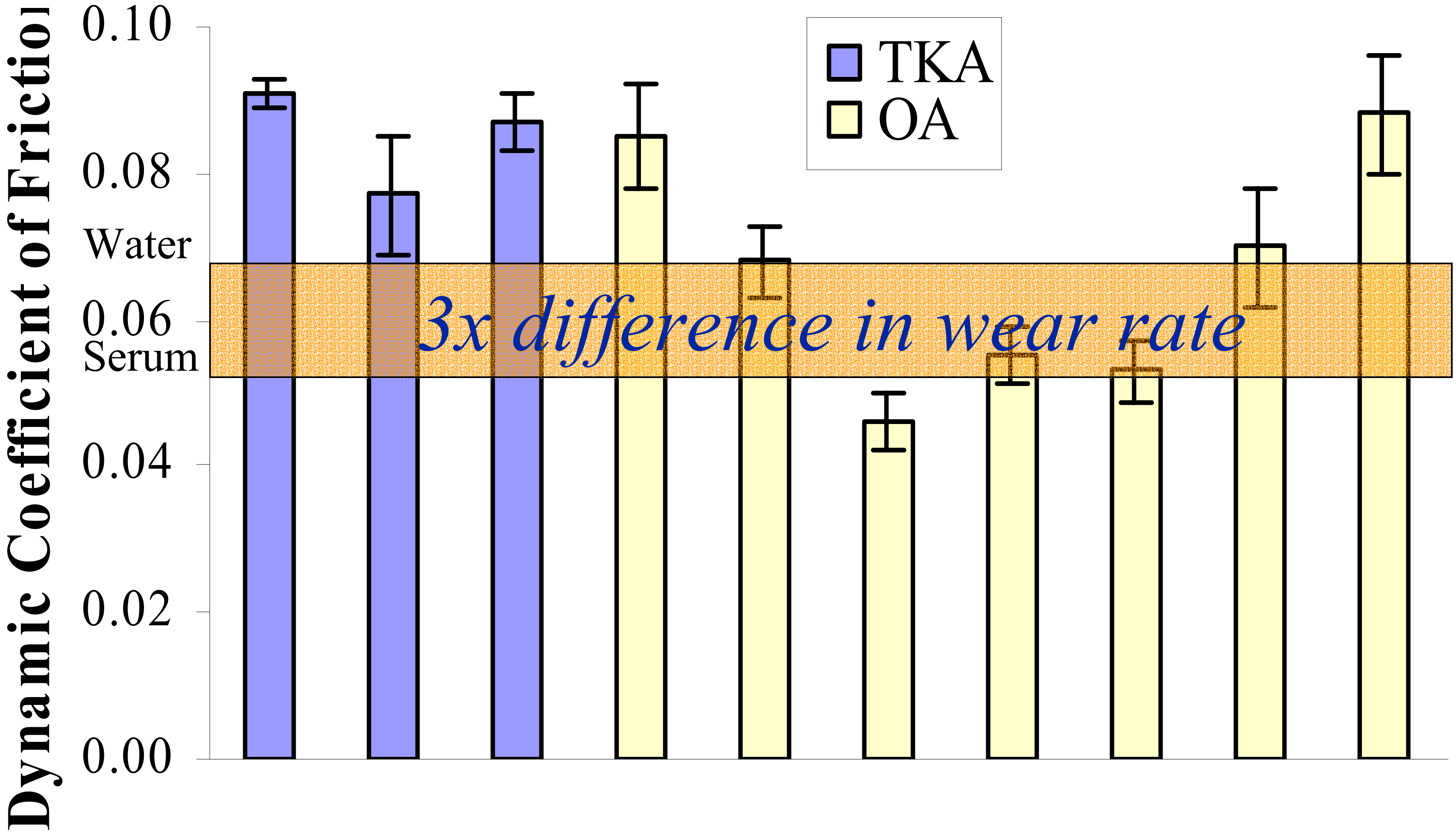
Oxinium versus CoCr Alloy for All Lubricants



Mazzucco & Spector

2-factor ANOVA; $p<0.0001$; power=1

Results: Joint Fluid Lubrication



Within each group, samples are arranged in the order they were obtained

Bars represent standard deviation

Mazzucco & Spector

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- Non-allergenic

Decrease in the Stress in the Distal Femur after TKA due to the Stiffness of the Co-Cr Femoral Component: Finite Element Analysis

Image removed due to copyright considerations.

M. Angelides, *et al*., Trans. Orthop. Res. Soc., 13:475 (1988)

Bone Loss due to Stress Shielding under a Femoral Component: Canine Model

Image removed due to copyright considerations.

J.D. Bobyn, *et al.*, Clin. Orthop., 166:301 (1982)

RADIOGRAPHIC BONE LOSS AFTER TKA*

- Retrospective radiographic analysis of 147 TKAs.
  - 3 designs
  - Cemented and porous-coated, non-cemented
- Determination of whether bone loss was evident in the post-op radiographs.
  - 3 examiners

* Mintzer CM, Robertson DD, Rackemann S, Ewald FC, Scott RD, Spector M. Bone loss in the distal anterior femur after total knee arthroplasty. Clin Orthop. 260:135 (1990)

Bone Loss After TKA: Radiographic Study

Sites at which changes in bone density was evaluated.

Image removed due to copyright considerations.

Image removed due to copyright considerations.

C.M. Mintzer, *et al*., Clin Orthop. 260:135 (1990)

Bone Loss Under the Femoral Component of a Total Knee Replacement Prosthesis: Stress Shielding

1 year post-op

Image removed due to copyright considerations.

Image removed due to copyright considerations.

C.M. Mintzer, *et al.*, Clin Orthop. 260:135 (1990)

BONE LOSS UNDER THE FEMORAL COMPONENT OF TKA

- Bone loss occurred in the majority of cases (68% of patients).
- Bone loss occurred within the first post-operative year and did not appear to progress.
- Bone loss was independent of implant design and mode of fixation (*i.e.*, cemented vs. non-cemented).

C.M. Mintzer, *et al.*, Clin Orthop. 260:135 (1990)

EFFECT OF BONE LOSS ON BONE STRENGTH

How much bone loss needs to occur before it is detectable in a radiograph?

- Radiographic evidence of bone loss in the distal femur = 30% reduction in bone density.*

How does bone loss affect bone strength?

- Bone strength is proportional to density^2.
- Therefore a 30% decrease in bone density means a 50% decrease in bone strength.

*D.D. Robertson *et al*., J. Bone Jt. Surg. 76-A:66 (1994)

BONE LOSS UNDER THE FEMORAL COMPONENT OF TKA

Conclusion

- Bone loss occurs in the distal anterior femur post-TKA due to stress shielding related to the stiffness of the cobalt-chromium alloy component

C.M. Mintzer, *et al.*, Clin Orthop. 260:135 (1990)

BONE LOSS DUE TO STRESS SHIELDING

Potential Problems

- Complicates revision arthroplasty due to the loss of bone stock.
- May place the prosthesis at risk for loosening.
- May place the distal femur at risk of fracture.

Solution

- Oxinium TKA.
  - Oxinium has approximately ½ the stiffness of Co-Cr alloy, therefore there should be less stress shielding and less bone loss.

ADVANTAGES OF OXINIUM

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- Much lower modulus than Co-Cr alloy (similar to Ti): lower stiffness and less stress shielding
- Non-allergenic

METAL SENSITIVITY IN PATIENTS

- 10-15% of population have dermal sensitivity to metal (14% to Ni)
- Metals known as sensitizers:
  - Ni > Co and Cr >>> Ti and V
- 60% of pts. with failed TJRs were metal sensitive vs. 25% with well-functioning implants
  - Did metal sensitivity cause failure or did the failed implant cause metal sensitivity?

Hallab, Merritt, Jacobs, JBJS 83-A:428 (2001)

WHAT ARE CERAMICS?

- Compounds of metallic and nonmetallic (*e.g.*, oxygen) elements.
- Ceramic materials:
  - Alumina (aluminum oxide)
  - Zirconia (zirconium oxide)
- Metal oxides on metallic materials:
  - Chromium oxide (on Stainless Steel and Co-Cr alloys)
  - Titanium oxide (on Titanium and Titanium alloy)
  - Zirconium oxide (on Zr-Nb alloy)

ADVANTAGES OF CERAMICS

- **Dense/hard (scratch resistant)**

  Related to the character of the ionic bonding

- **Ability to be polished to an ultra smooth finish**

CHARACTERISTICS OF OXIDES THAT AFFECT THEIR PERFORMANCE

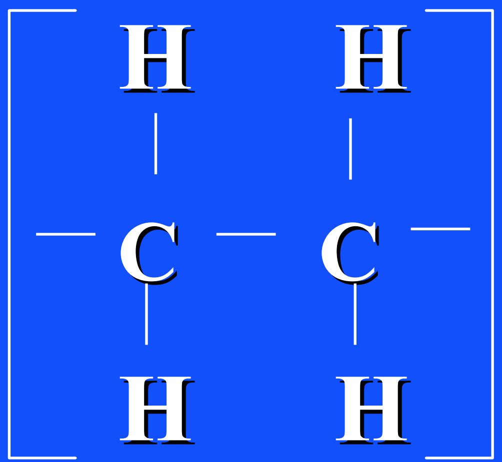
- **Adherence to metal substrate**

  Related to the mismatch in bonding (oxides comprise ionic and covalent bonds in contrast to metallic bonds)

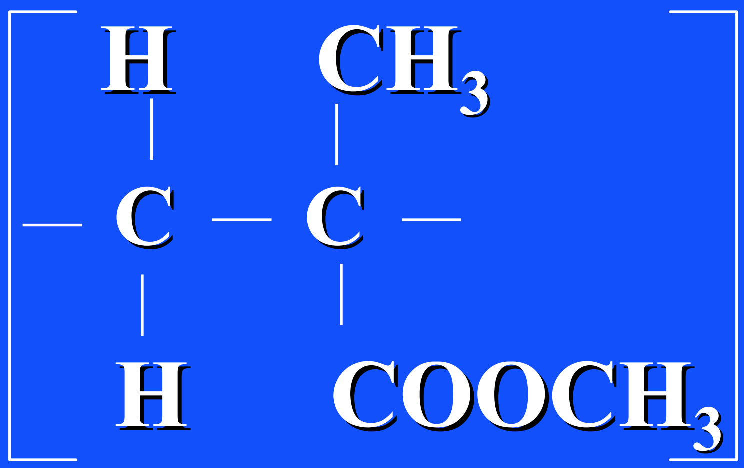
- **Porosity/density**
- **Thickness**

POLYMERS

Polyethylene



Polymethylmethacrylate



ORTHOPEDIC POLYMERS

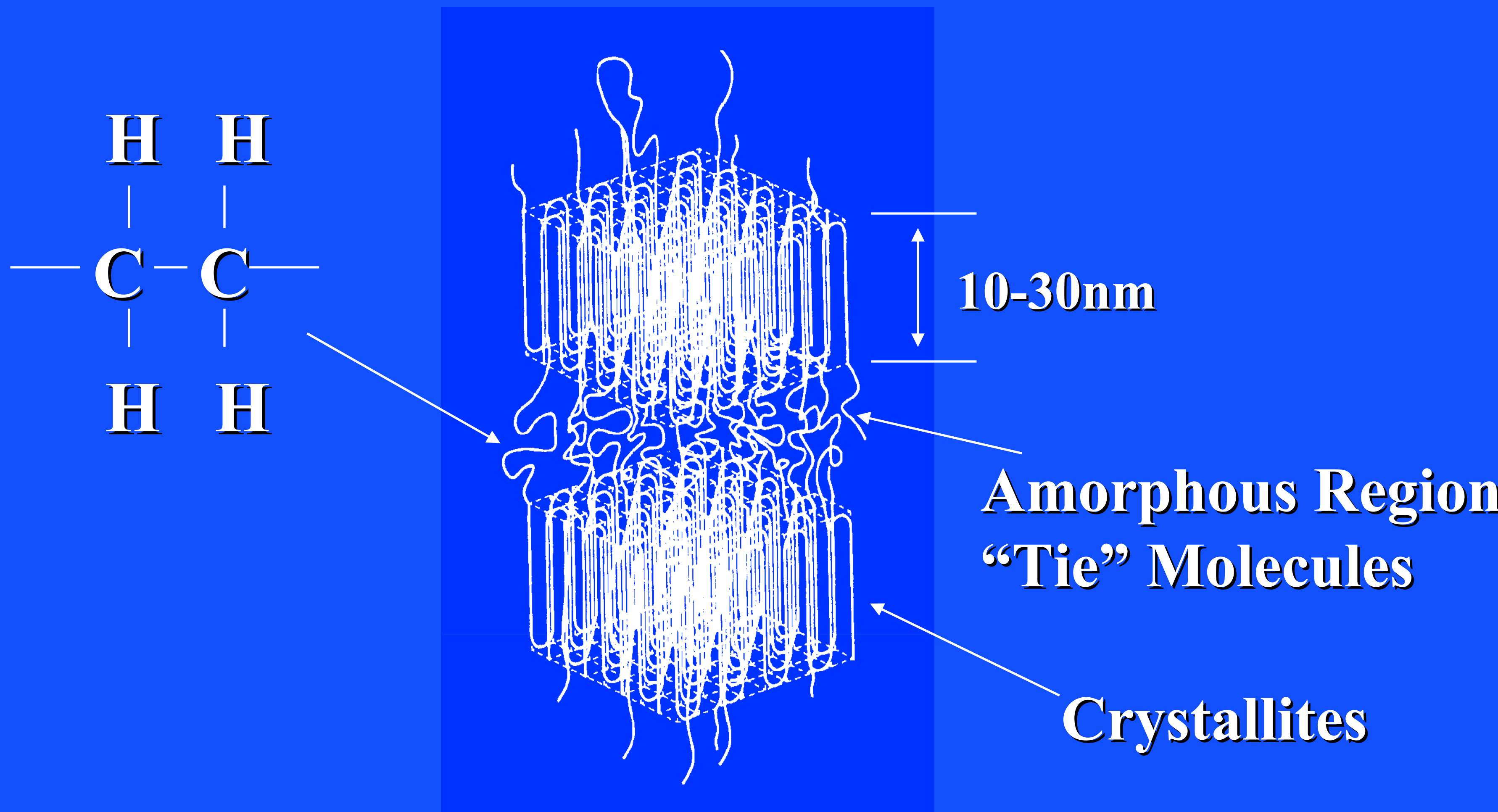
	ADVANTAGES	DISADVANTAGES
UHMWPE	Relatively high wear resistance	Subject to oxidation
PMMA	Polymerization *in vivo*	Low fatigue strength (for load-bearing applications)

MOLECULAR STRUCTURE OF POLYETHYLENE

Micrometer Level

Fusion defects due to incomplete consolidation are cracks that can be propagated by fatigue (delamination) wear.

ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE



MOLECULAR STRUCTURE OF POLYETHYLENE

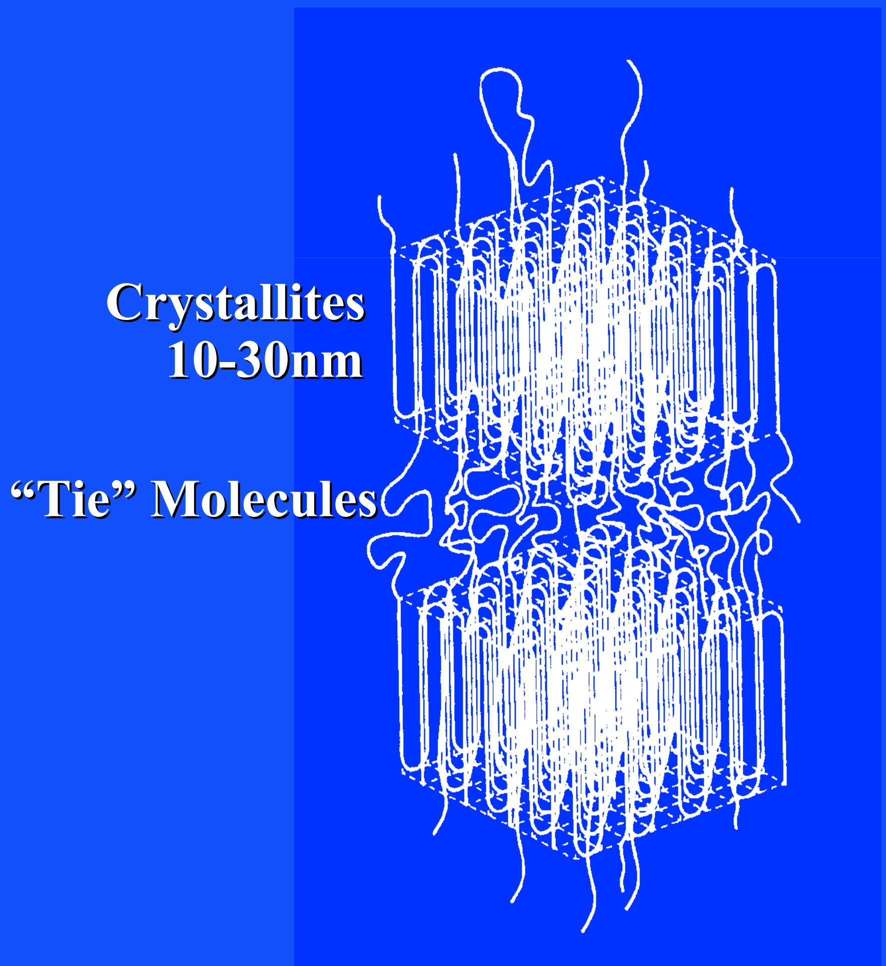
Nanometer Level

- "Tie" molecules bind PE crystallites
- Mechanical properties are related to the number of tie molecules (fracture occurs through the amorphous region comprised of tie molecules)
- Mechanical bonding between PE particles is due to entanglement of molecular chains
- Reinforcing elements (*e.g.*, fibers) added to PE are only effective if PE bonds to them

POLYETHYLENE WEAR AND STRENGTH

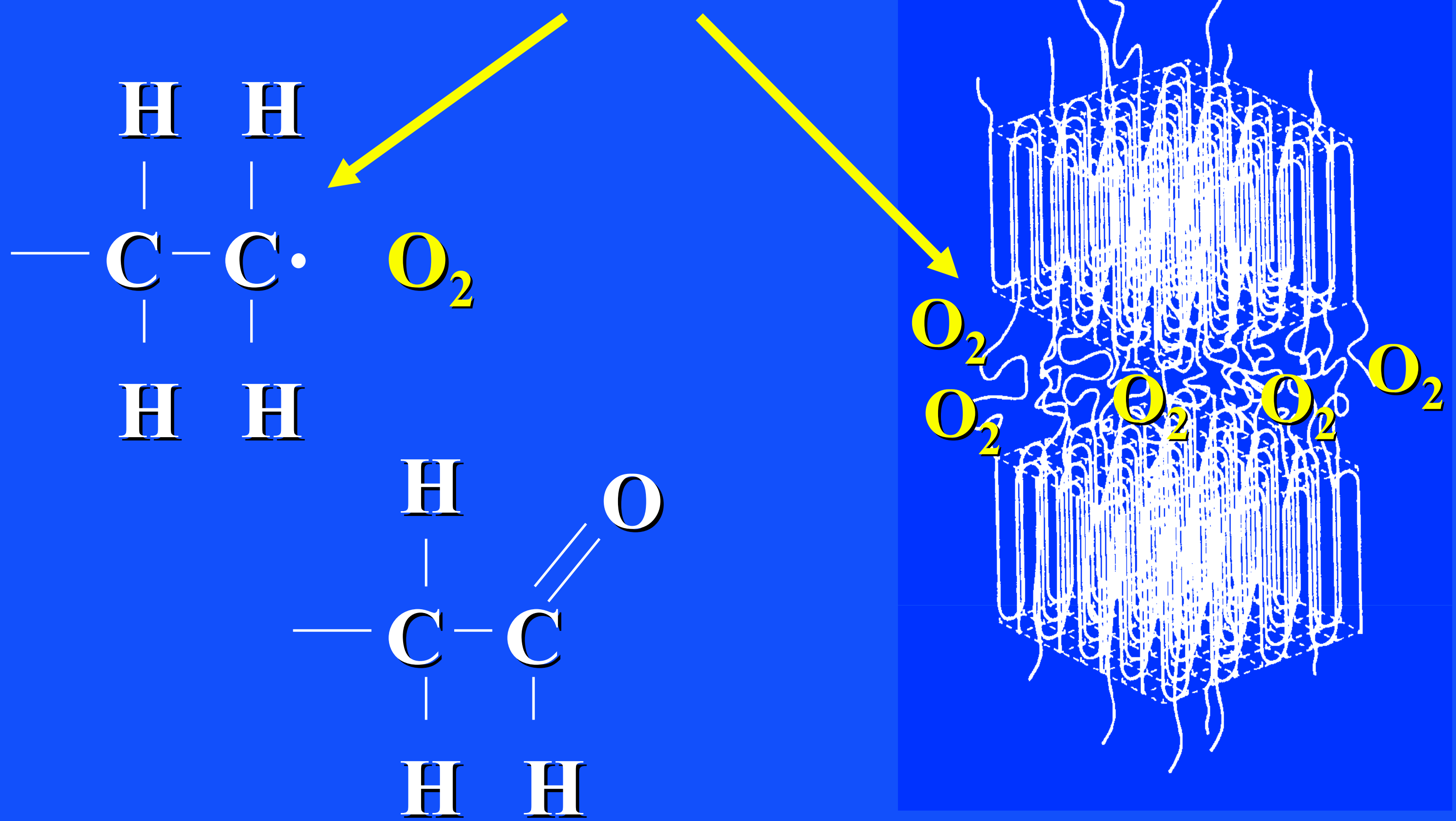
Intrinsic Factors

- Molecular weight distribution
- Cross-linking
- Crystallite size, shape, and orientation
- Degree of crystallinity
- Number of tie molecules



EFFECT OF GAMMA RADIATION ON PE: OXIDATION

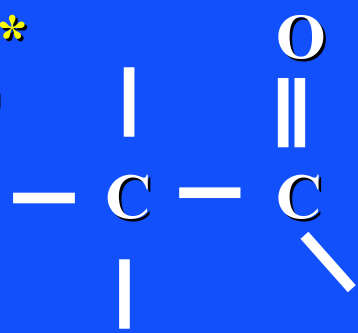
Gamma Radiation



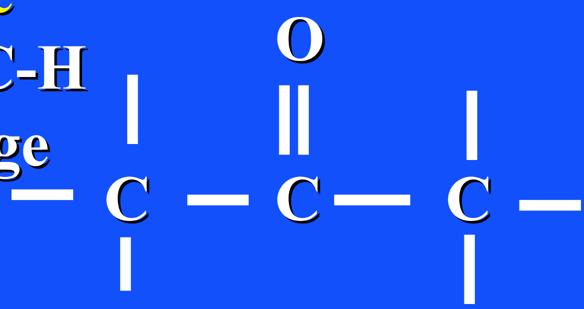
GAMMA-RADIATION INDUCED MODIFICATION OF POLYETHYLENE

Oxidation

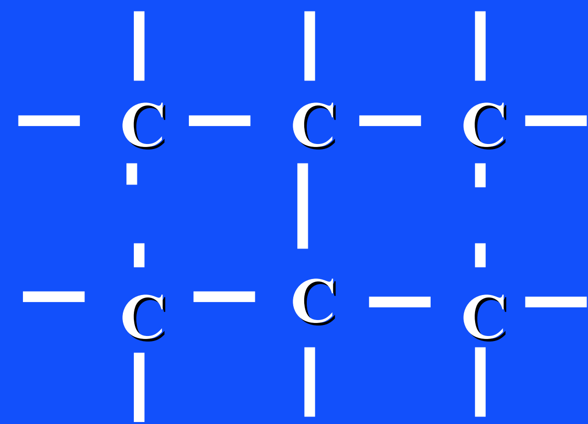
Aldehyde*
from C-C
cleavage



Ketone**
from C-H
cleavage



Cross-linking



from C-H
cleavage

* Small peak in IR
**Large peak in IR

Image removed due to copyright considerations

From Sutula, Sperling, Collier, Saum, Williams. “Delamination and White Band: Impact of Gamma Sterilization in Air and Material Consolidation” AAOS 1995 Orlando