

Ductility Enhancement of Mo Phase by Nano-sized Oxided Dispersions

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The overall research objective is to understand and tailor the impurity effects for room-temperature ductility improvement of Mo- and Cr-based alloys by the inclusion of suitable nano-sized metal oxide dispersions.

Task 1: Atomistic Modeling

To study **microscopic** mechanisms of impurity embrittlement of Mo- and Cr-based alloys and their room-temperature ductility enhancement effects of MgO or MgAl₂O₄.

Task 2: In-situ Mechanical Property Measurement

To develop a micro-indentation measurement technique for quick assessment of material mechanical properties.

Background

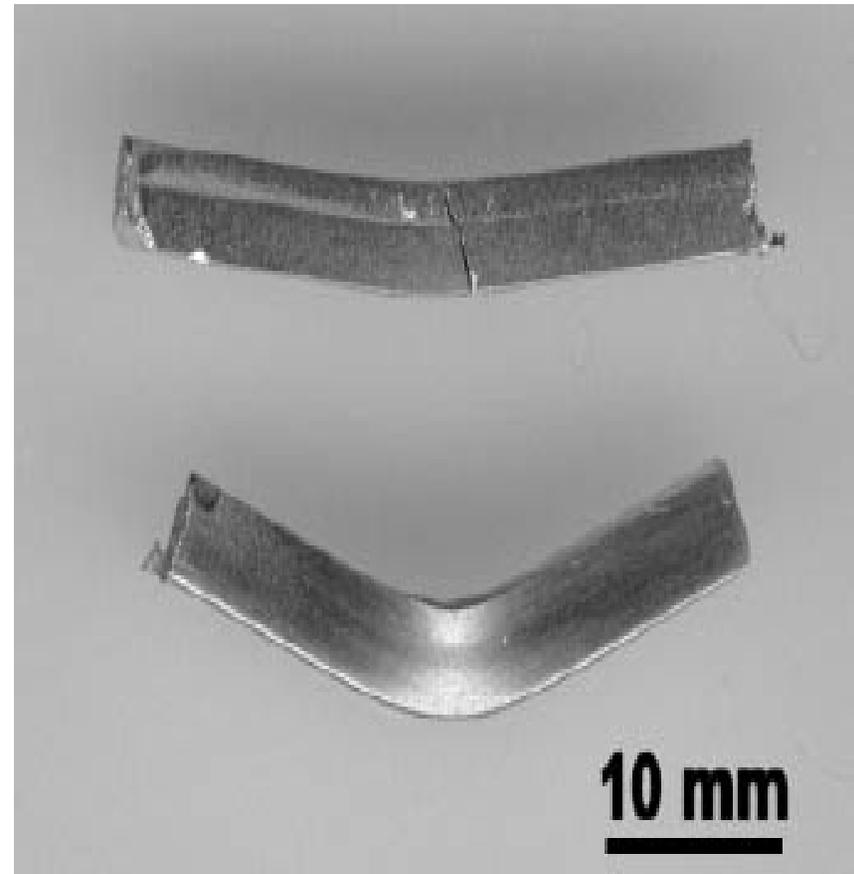
Due to their ultra-high working temperature (>1000oC) and excellent oxidation and corrosion resistance, a number of Cr and Mo based alloys are being developed as the next generation structural materials for fossil energy applications. However, a severe drawback with these materials is their limited room temperature ductility.

Past studeis showed ductility improvement of Mo phase by inclusion of metal oxide dispersion (e.g. Schnibel 2003)

Experimental difficulties:

- Optimal dispersion **composition**
 - $MgAl_2O_4$, MgO , or other oxide candidates?
 - nano-size oxide? how to achieve uniform dispersion and prevent agglomeration?

Atomistic modeling can provide some answers to these questions to reduce experimental trial and error



Mo with spinel dispersions: different procedures yield different results. (Schnibel, 2003)

Influence of impurity elements

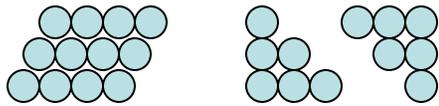
Insufficient ductility mostly due to impurities (such as N, O, etc.)

- weaken the metal-metal bond
- precipitate or segregate as brittle oxides or nitrides

Ductility enhancement by MgO or MgAl₂O₄ spinel dispersions:

- Scruggs 1965: on Cr and Mo Alloys
 - Mechanism assumed to be impurity gettering by spinel phase
- Brady 2003 (detailed microstructural analysis): on Cr Alloys
 - No gettering effect found (impurities not detected in oxide phase)
 - MgAl₂O₄ is not as effective as MgO
 - Other metal oxides were tried with detrimental results
 - unclear whether MgO or MgCr₂O₄ is more effective
 - **Fundamental mechanism remains unknown**
 - Difficult to optimize the composition and size of dispersion material

Rice's criterion



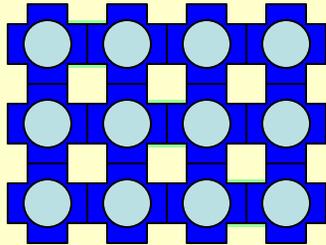
What matters are:

the characteristics of the **chemical bonds**

the properties of the **valence electrons**

How properties of electrons affect ductility

In brittle materials ...



○ ions
● electrons
○ voids

Localized, immobile electrons
form rigid bonds → **brittle**

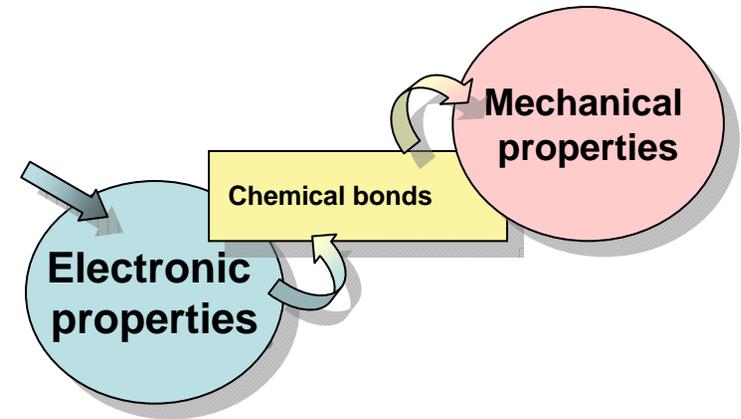
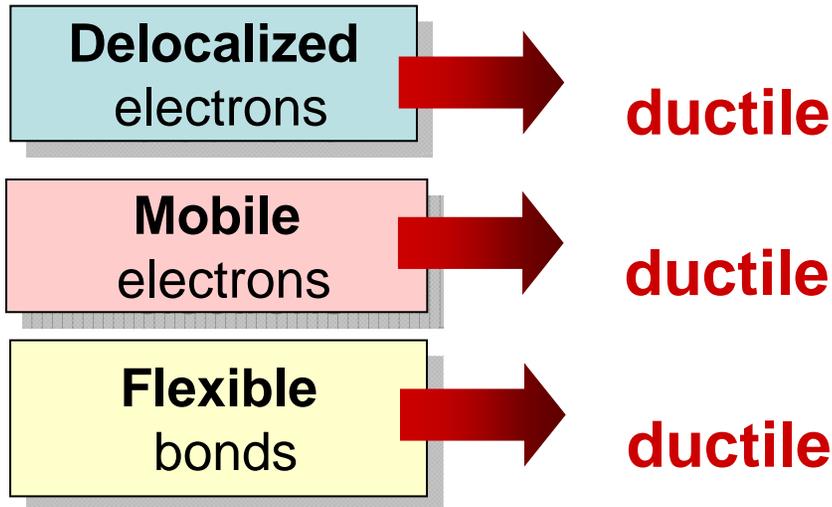
Localized around ions

Immoble (cannot fill the voids easily)

Delocalized, mobile electrons

make flexible bonds → **ductile**

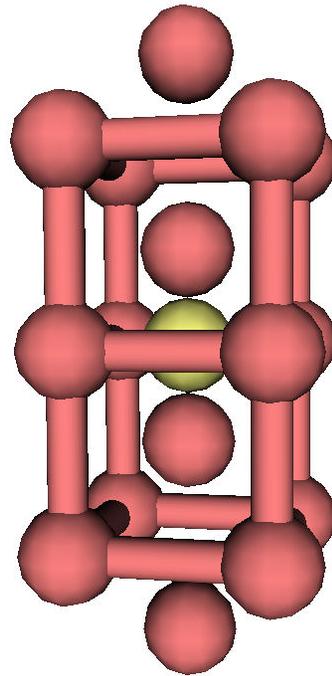
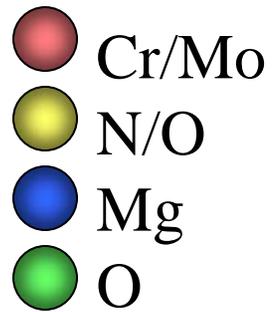
Rice's criterion



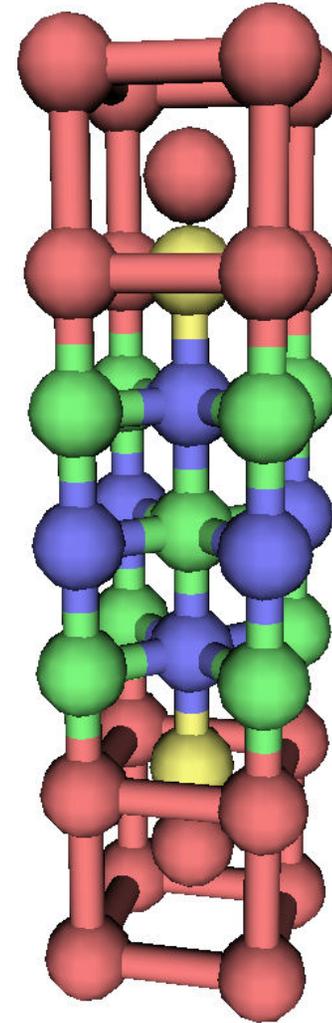
Properties of electrons

- **Space distribution**
How localized/delocalized electrons are
- **Energy distribution**
How easy electrons can be excited to mobile states
- **Angular momentum distribution**
How rigid/flexible chemical bonds are

Model systems

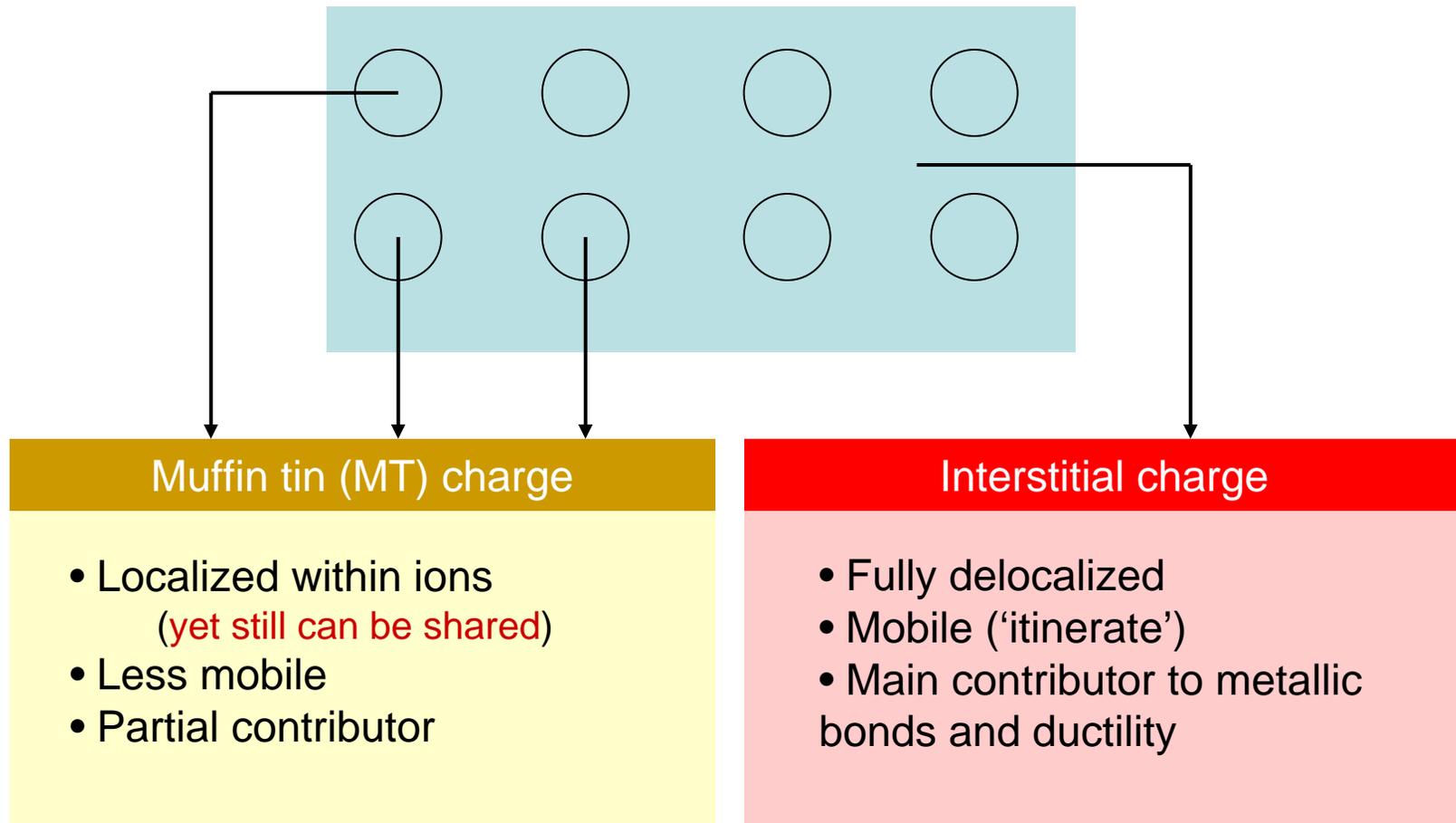


A. impurity embrittled system



B. ductility enhanced system

Charge density distribution

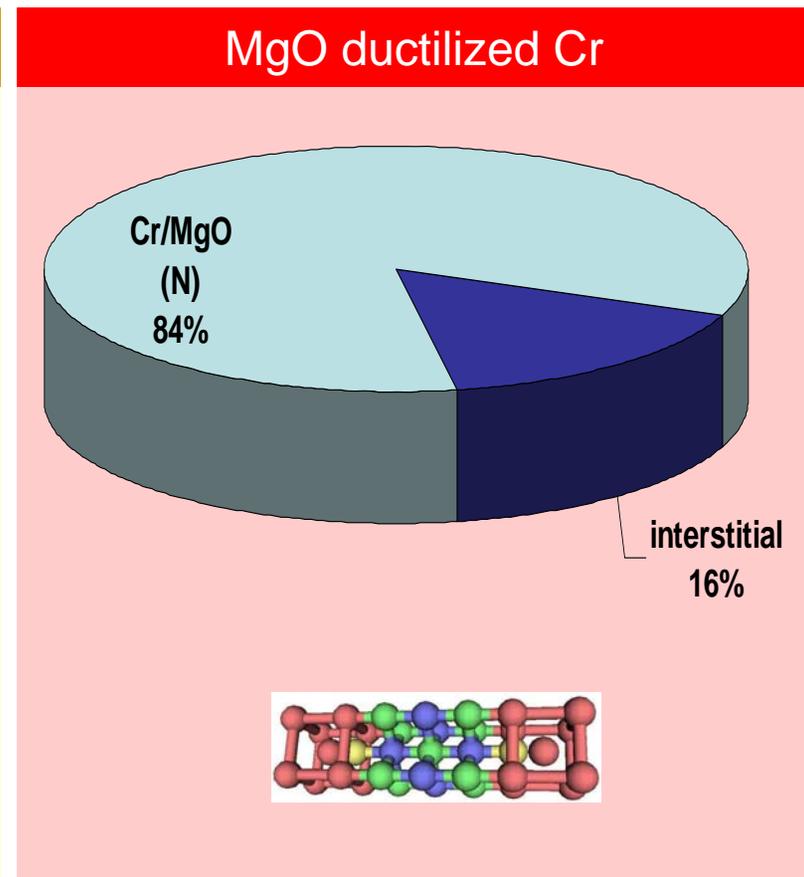
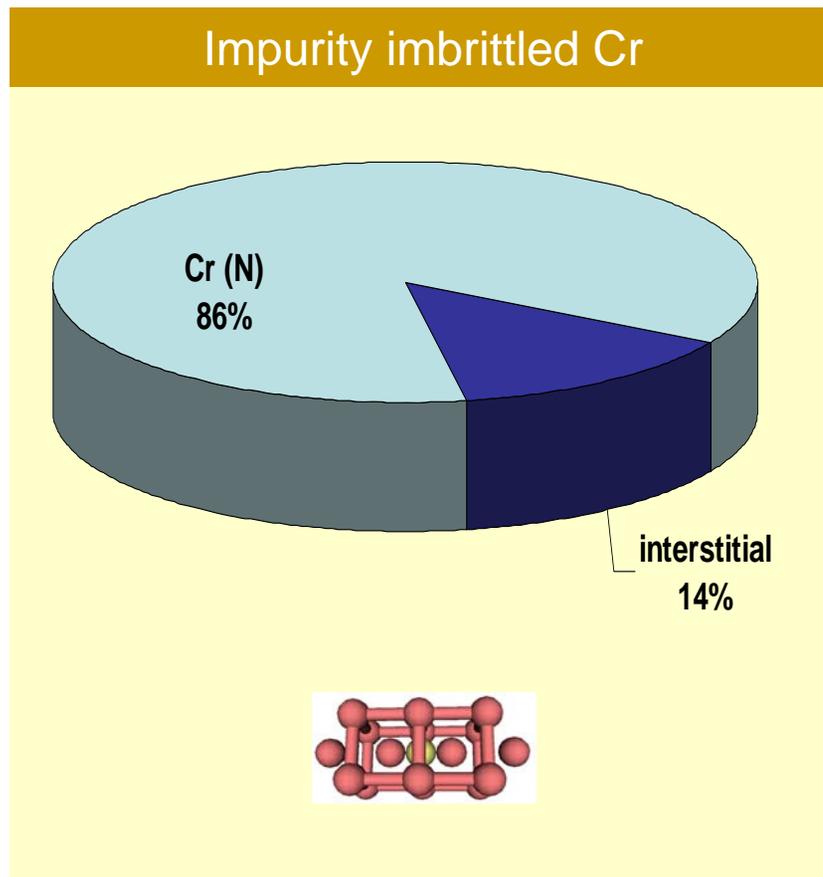


more **interstitial** charge
uniformly shared **MT** charge

→ **better ductility**
→ **better ductility**

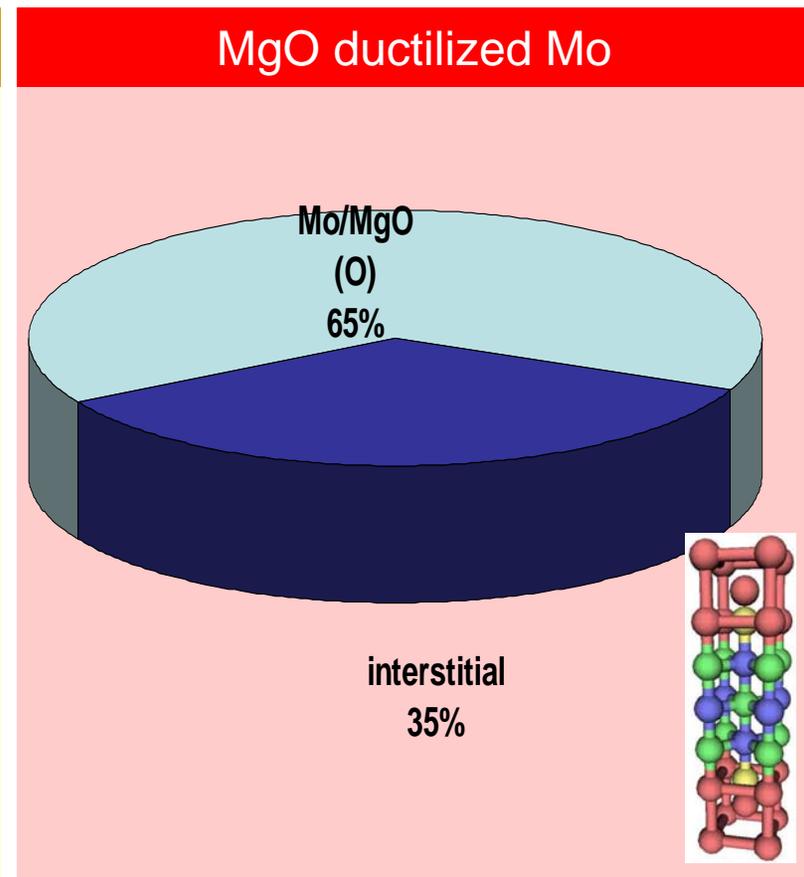
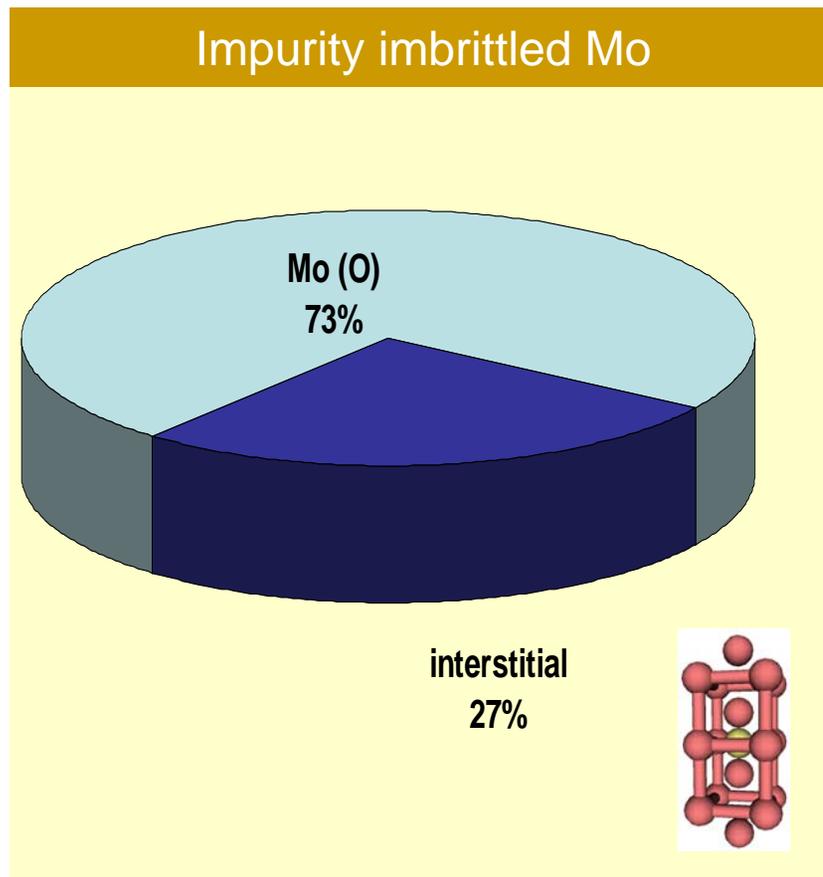
Results: Interstitial charge (Cr alloys)

more **interstitial** charge \rightarrow **better ductility**



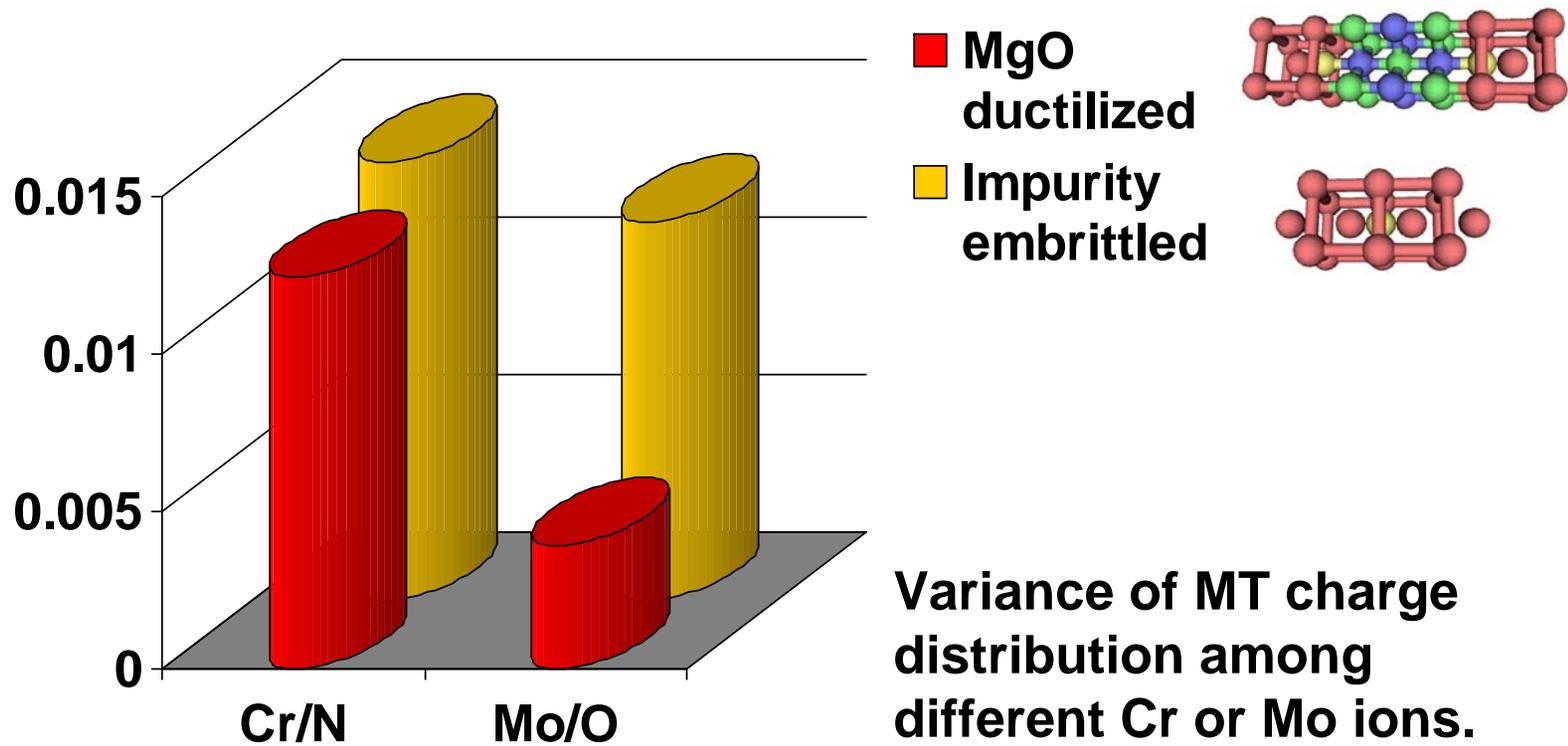
Results: Interstitial charge (Mo alloys)

more **interstitial** charge → **better ductility**



Results: Muffin-tin charge distribution

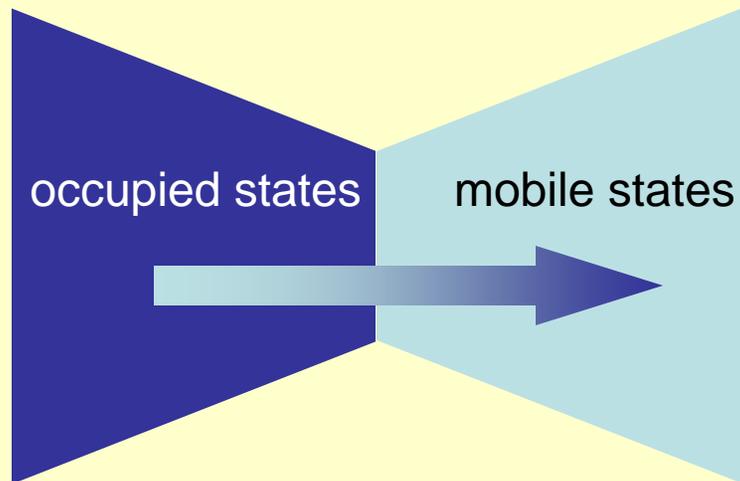
uniformly shared **MT** charge (less variance) → **better ductility**



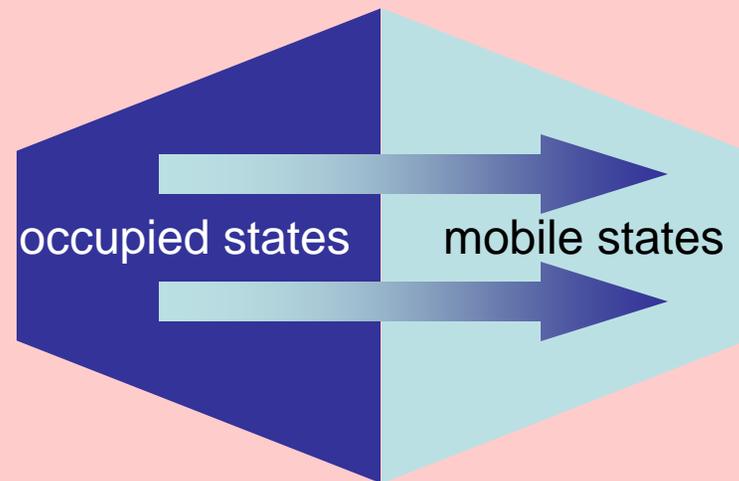
Density of states (DOS)

How **easy** electrons can cross the Fermi level to assume **mobile** states?

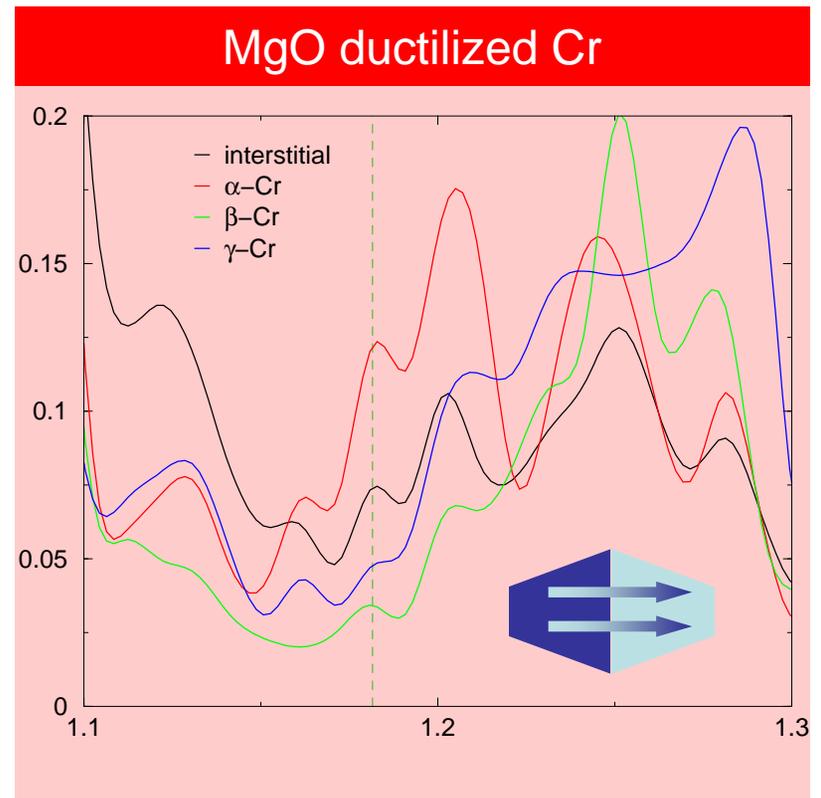
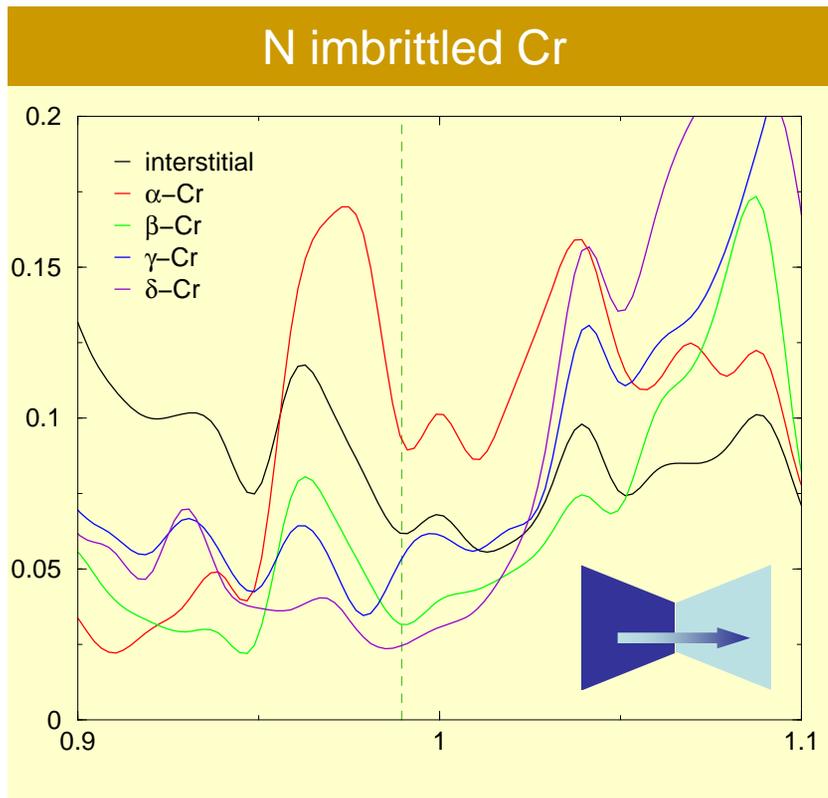
Narrow bottleneck: difficult



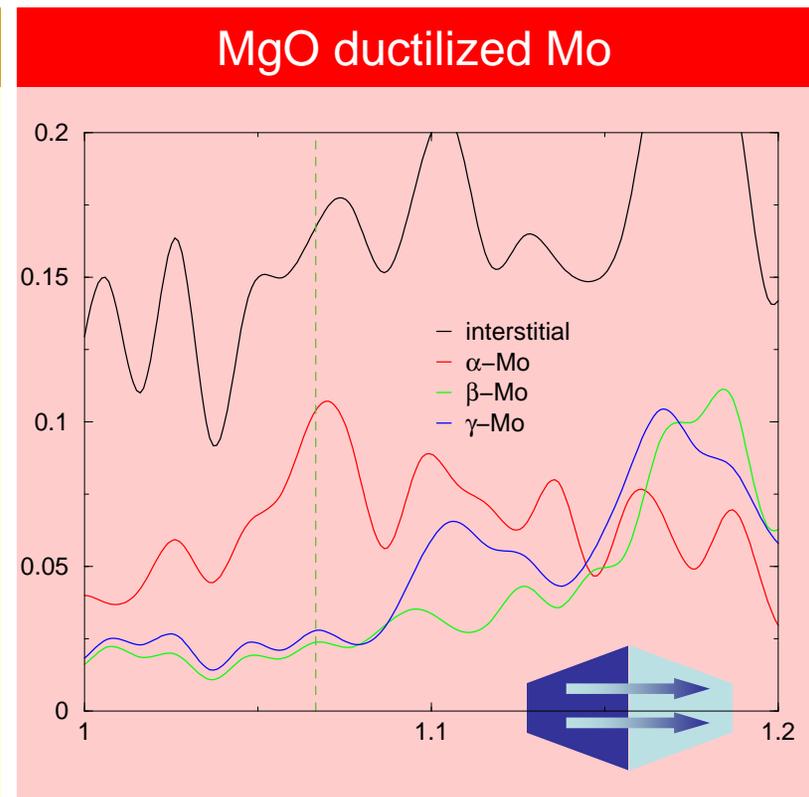
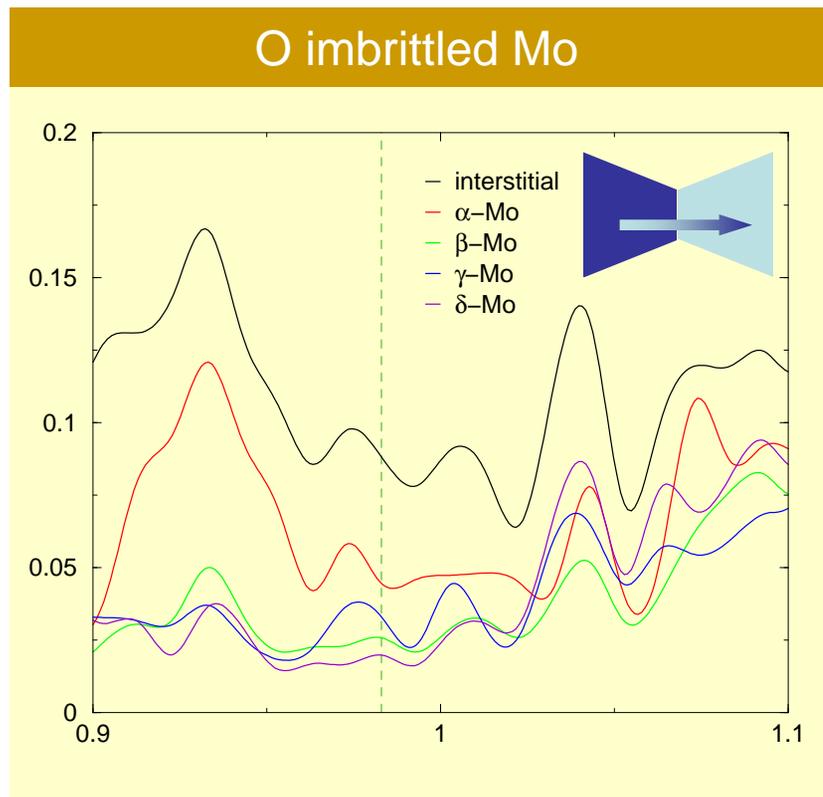
Wide connection: easy



Results: DOS (Cr alloys)

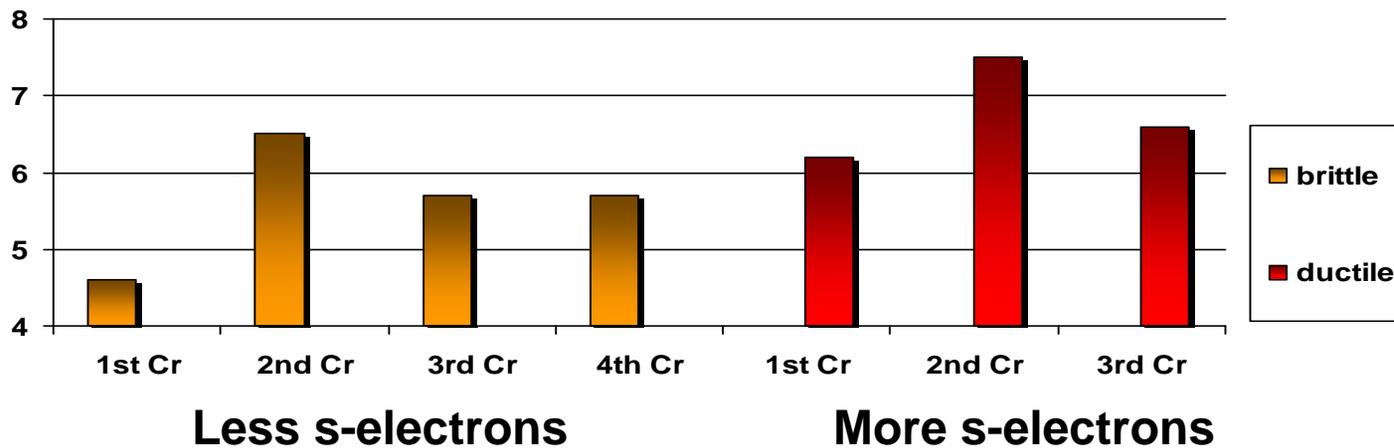


Results: DOS (Mo alloys)



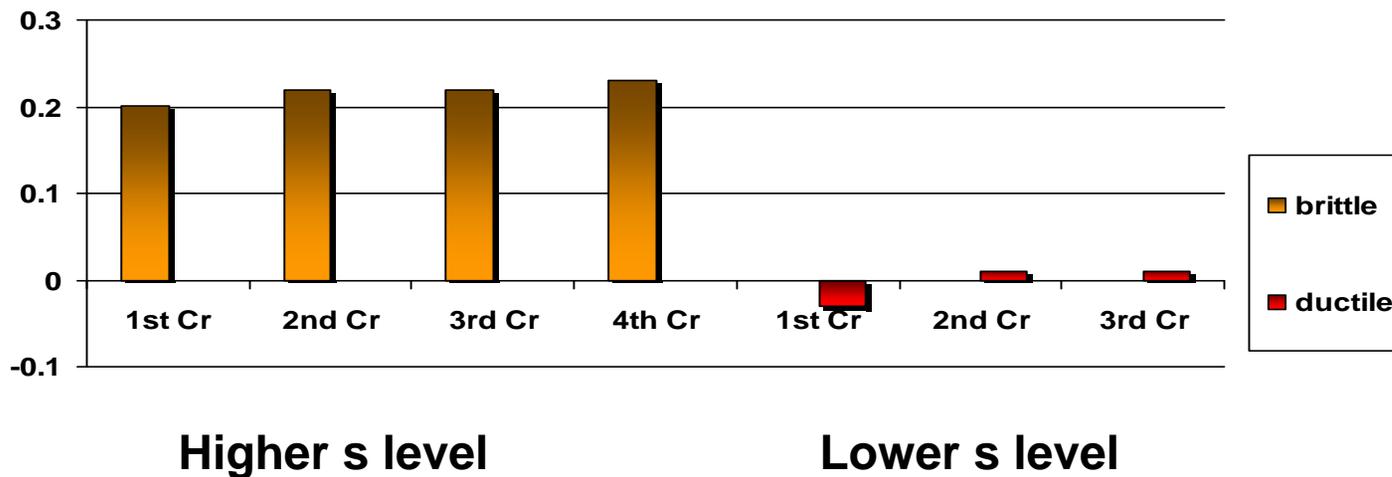
Results: L-projected population

Charge (e)	N imbrittled Cr				MgO ductilized Cr		
	1 st Cr	2 nd Cr	3 rd Cr	4 th Cr	1 st Cr	2 nd Cr	3 rd Cr
s-like	0.172	0.260	0.204	0.206	0.256	0.297	0.245
d-like	3.772	3.970	3.603	3.585	4.137	3.998	3.734
s/d %	4.6	6.5	5.7	5.7	6.2	7.5	6.6

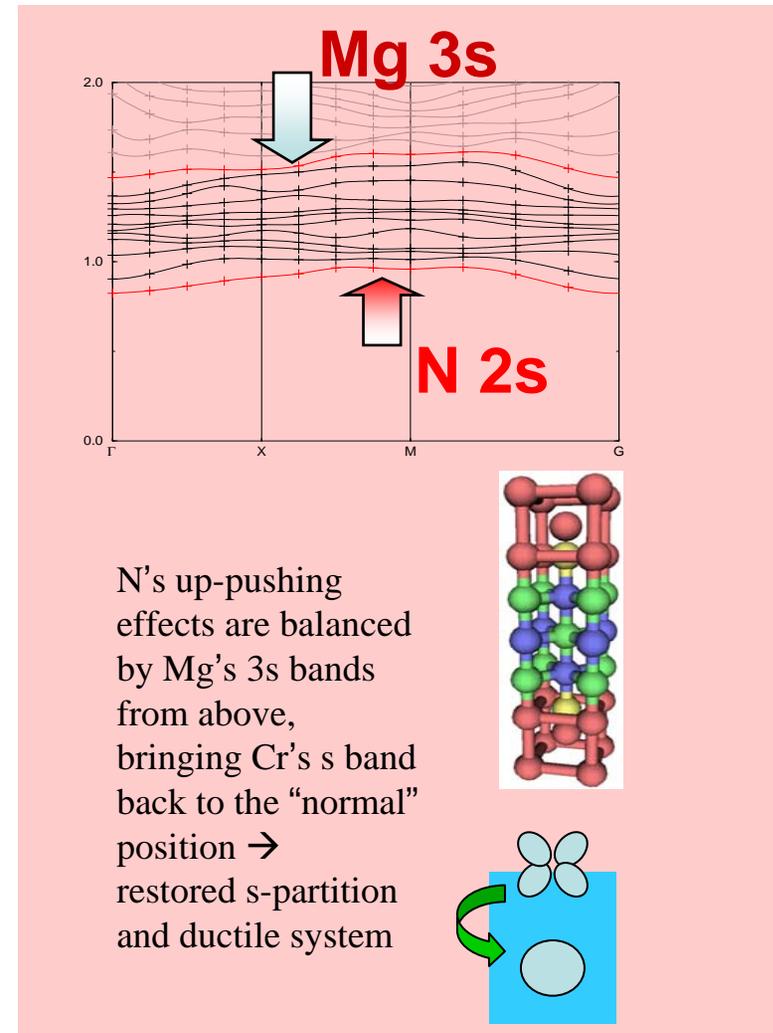
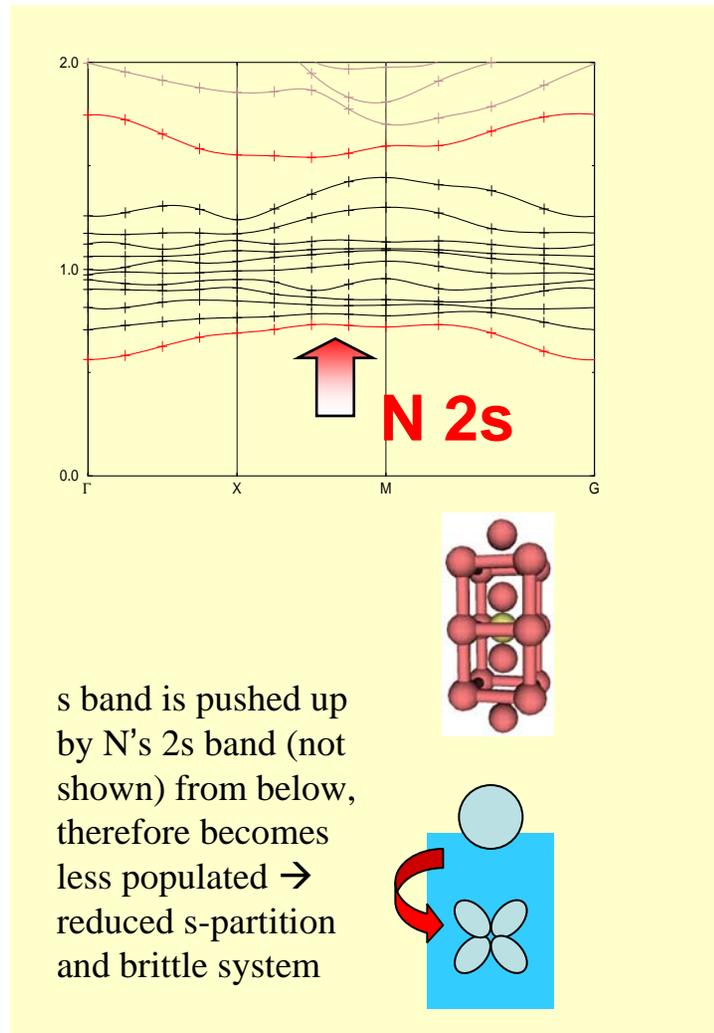


Results: L-projected energy

Energy Ryd.)	O embrittled Mo				MgO ductilized Mo		
	1st Cr	2nd Cr	3rd Cr	4th Cr	1st Cr	2nd Cr	3rd Cr
E* 4s	1.004	0.954	1.078	1.077	0.837	0.940	1.058
E* 3d	0.808	0.730	0.854	0.849	0.868	0.934	1.047
ΔE	0.20	0.22	0.22	0.23	-0.03	0.01	0.01



Results: Band structure



Summary: Properties of electrons

What has been achieved?

Identified **microscopic** criteria
to predict **brittle/ductile** properties

These criteria can

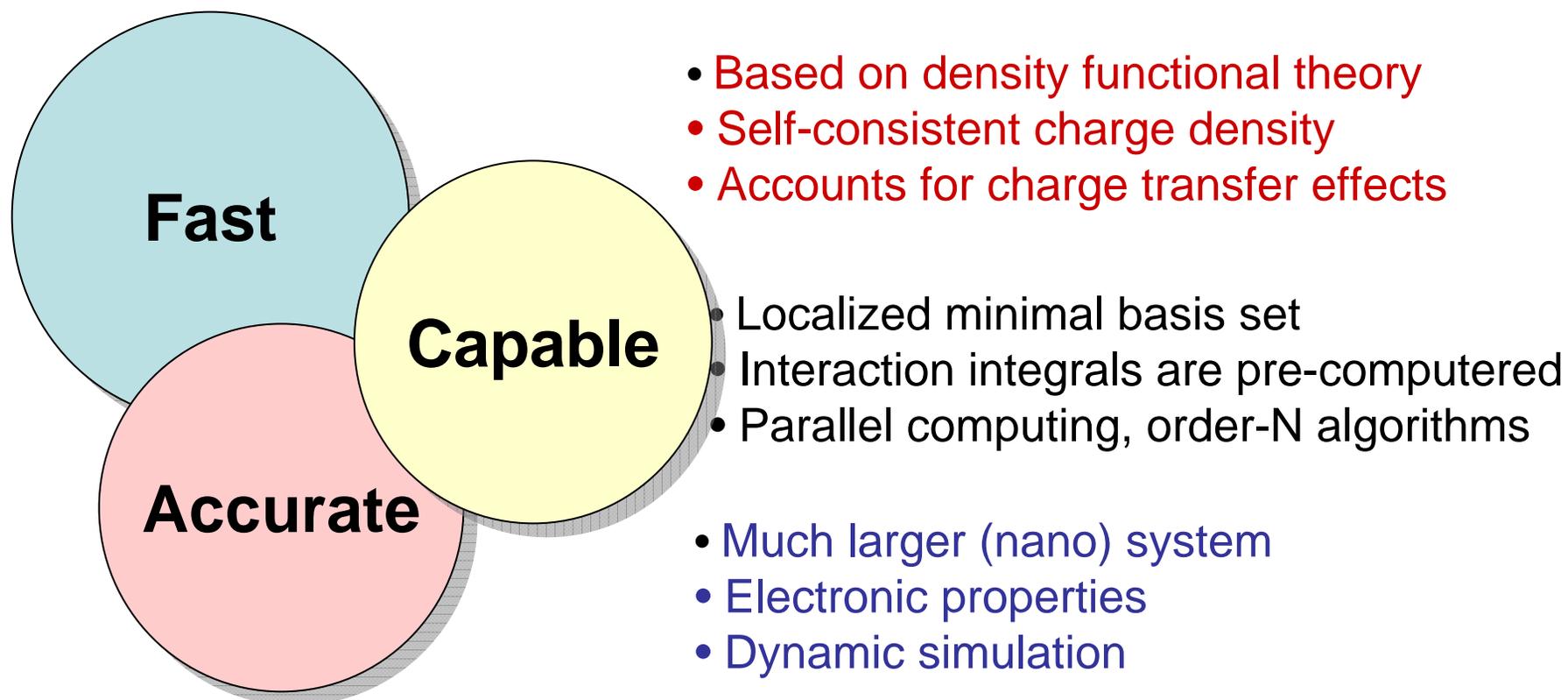
*Explain the **mechanism***

*Be used in larger scale simulations to **optimize** performance*

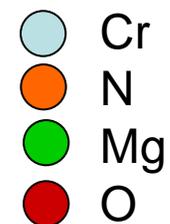
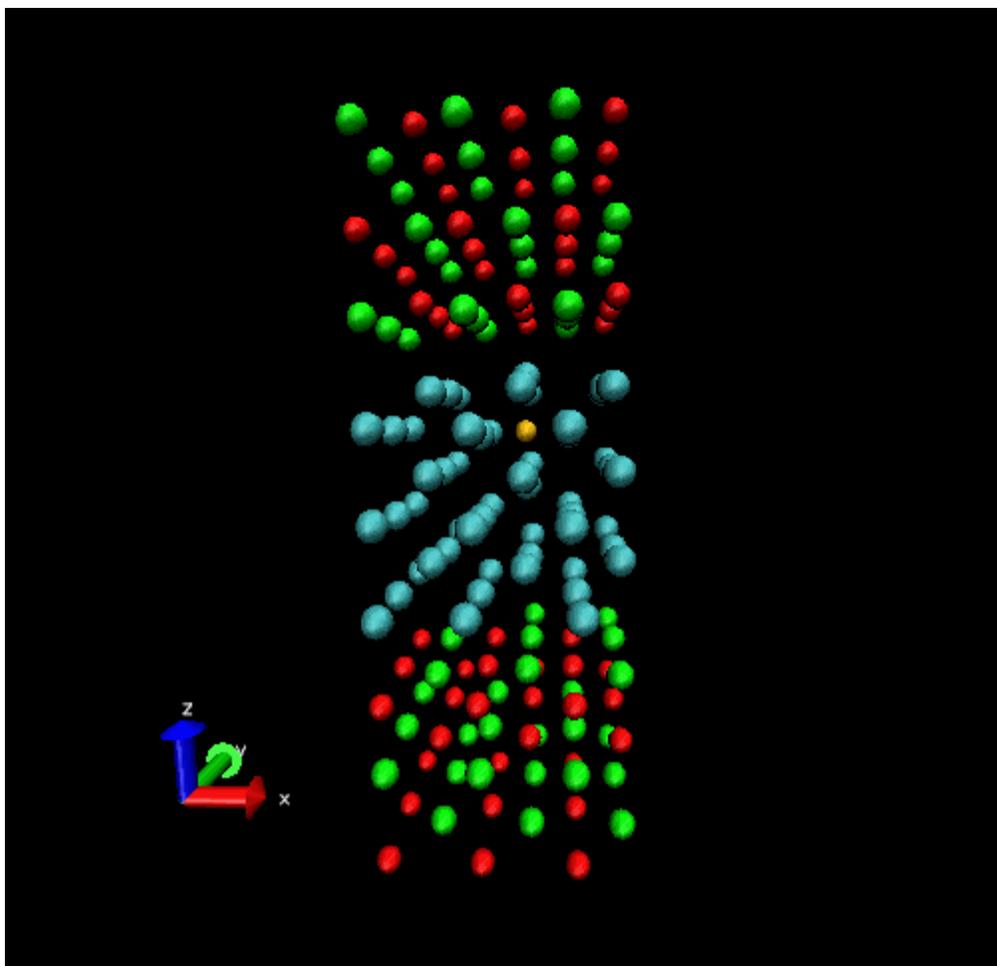
Molecular dynamics simulation: FIREBALL

Ab-initio tight-binding package

Lewis, Glaesemann, Voth, Fritsch, Demkov, Ortega, Sankey, Phys. Rev. B 64 (2001) 195103



Result: Molecular dynamics (Cr/MgO with N)



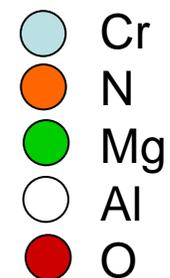
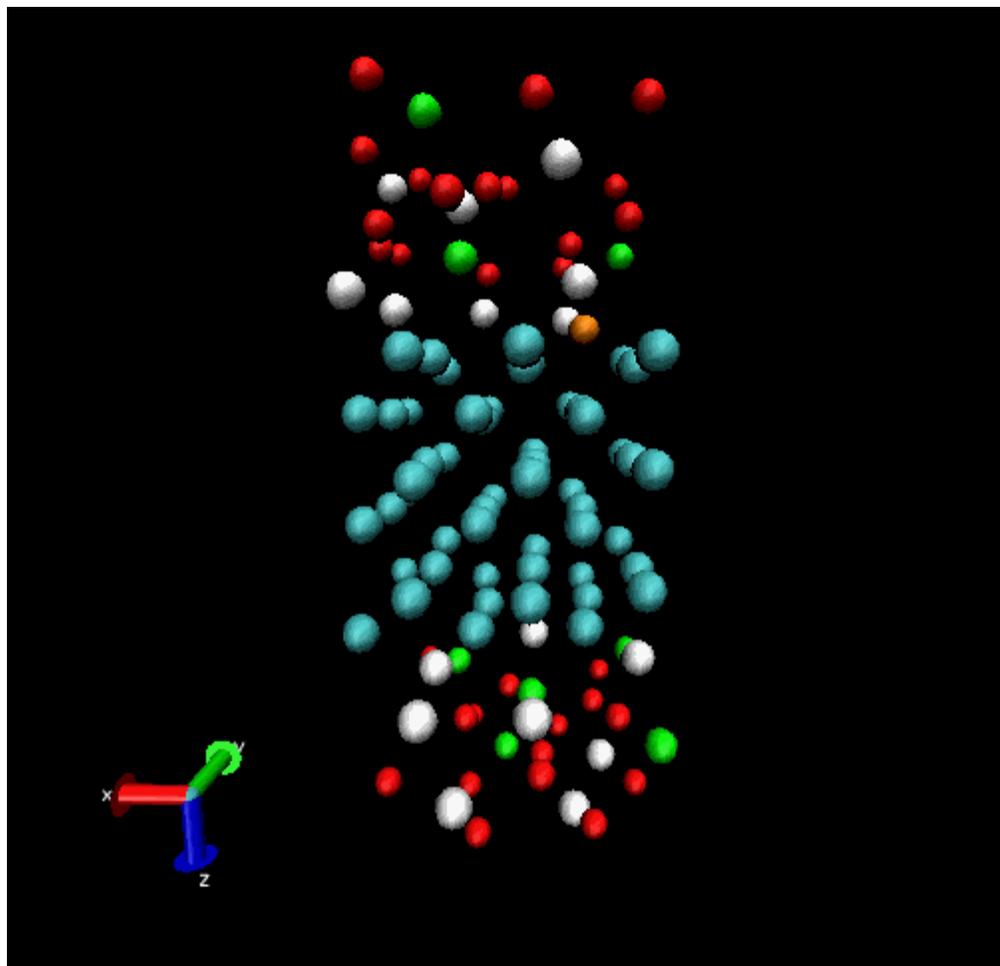
163 atoms

Constant Temperature
(600 K)

Diffusion time $\sim 1\text{ps}$ (10^{-12}s)
Diffusion length $\sim 2\text{\AA}$

Result consistent with
Brady's experiment

Result: Molecular dynamics (Cr/MgAl₂O₄ with N)

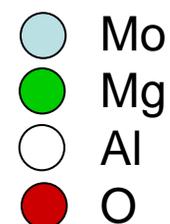
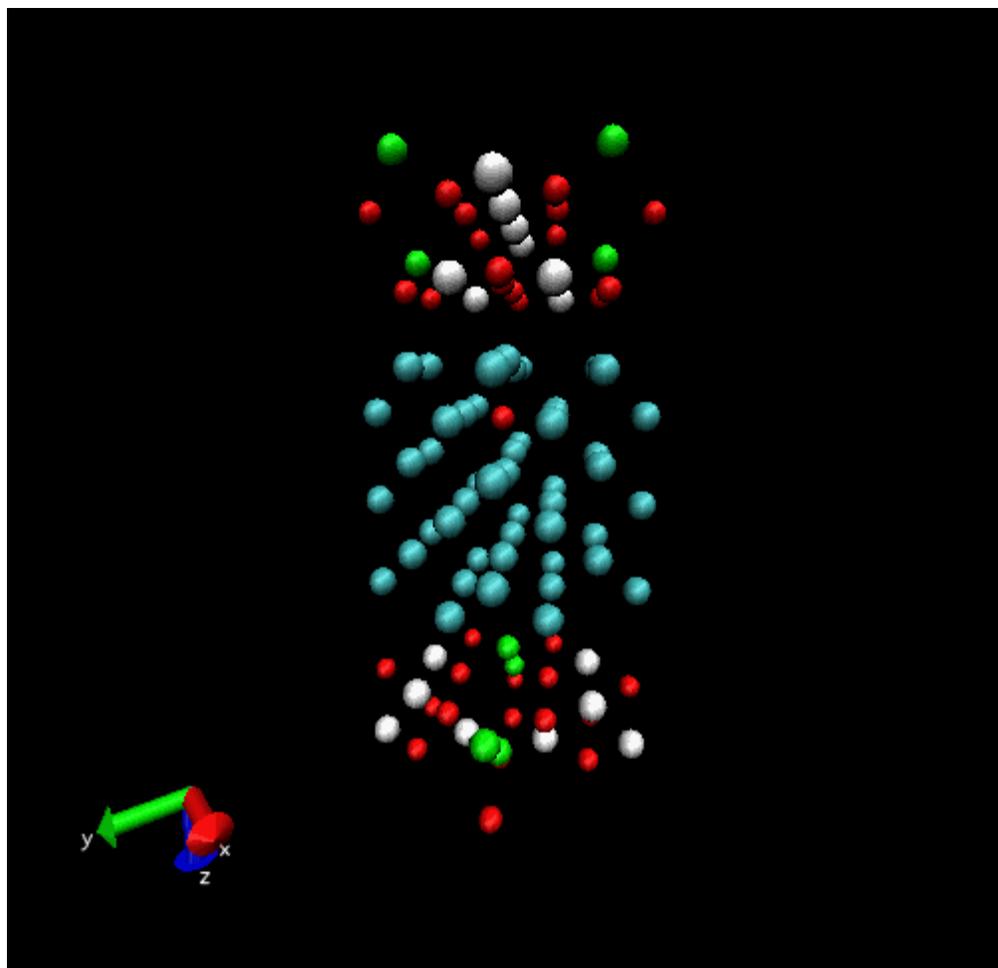


111 atoms

Constant Temperature
(600 K)

Diffusion time ~ 1 ps (10^{-12} s)
Diffusion length ~ 2 Å

Result: Molecular dynamics (Mo/MgAl₂O₄ with O)



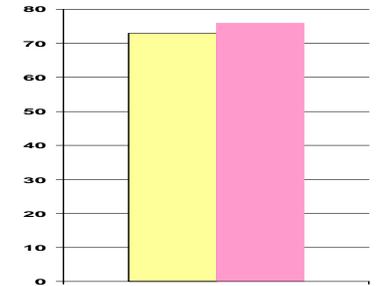
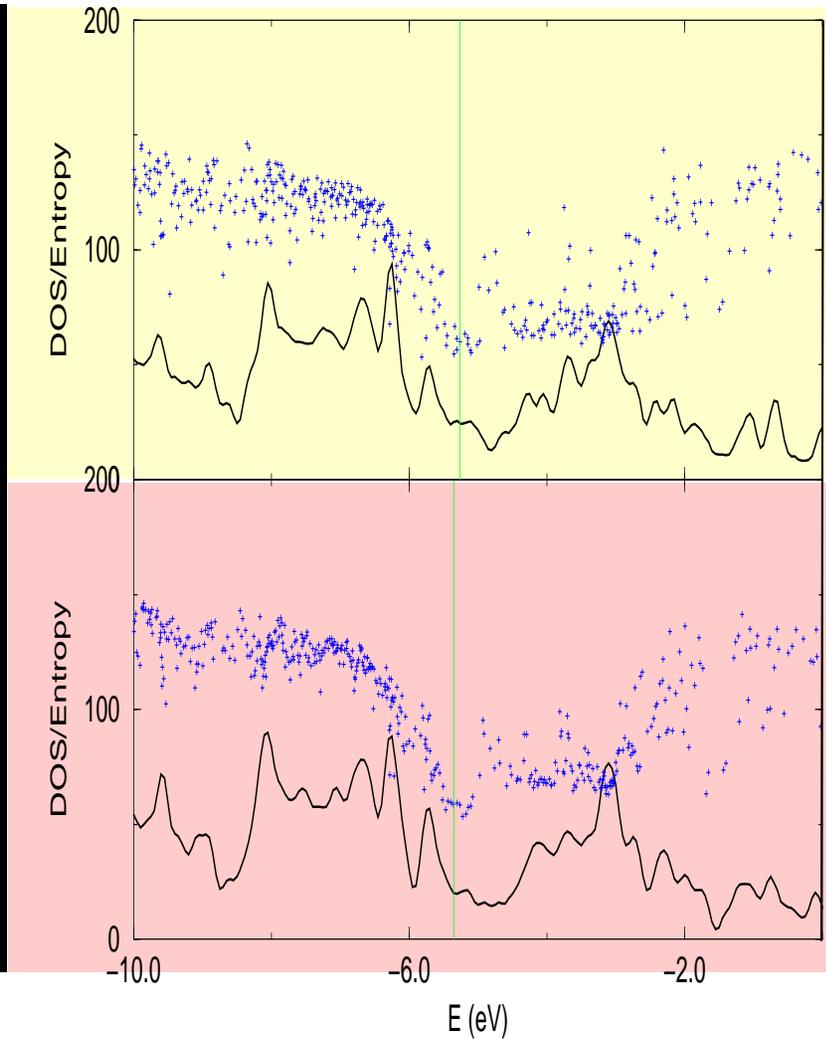
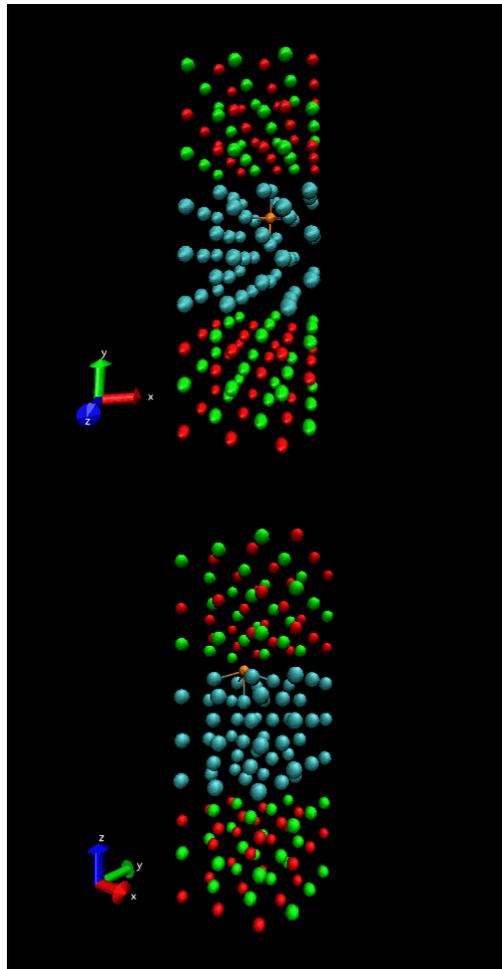
105 atoms

Constant Temperature
(600 K)

Simulation time ~1.6ps

No significant oxygen
diffusion is observed.
Results support
Schneibel's conclusion.

Analysis: Charge density distribution and DOS



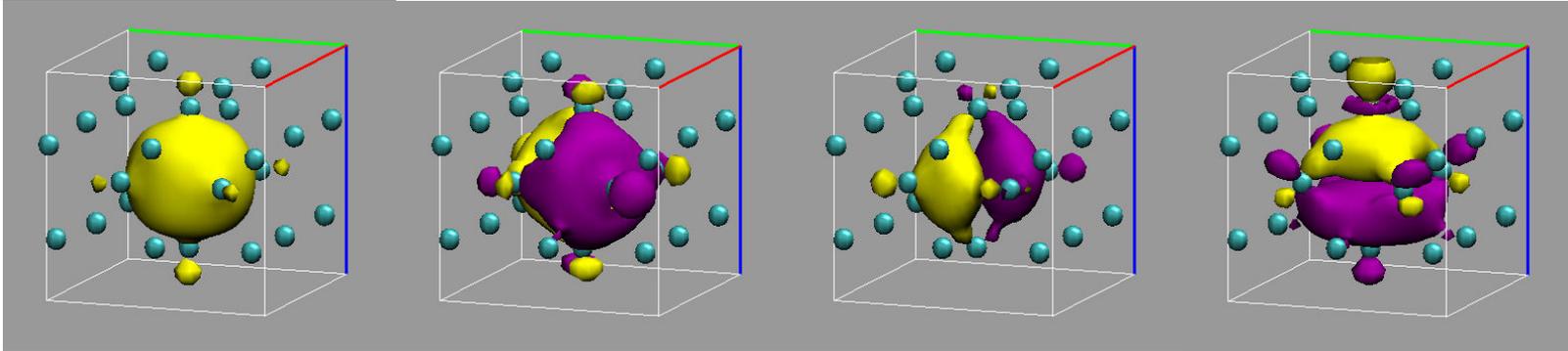
of states within +/- 1eV of Fermi level



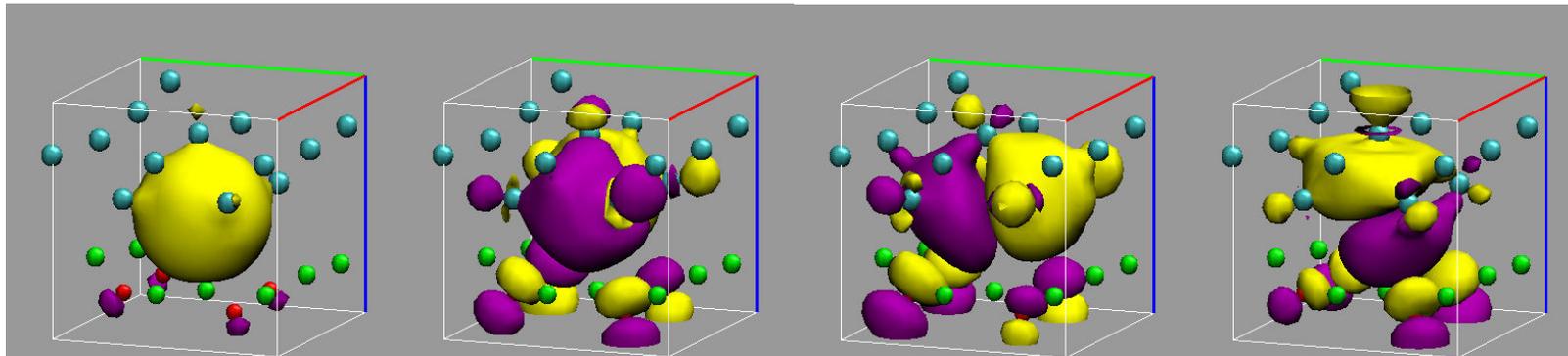
Avg. entropy

Analysis: Impurity electronic states

In the bulk of Cr



Near the Cr/MgO boundary



Conclusion: O-N antibonds force the impurity states to rotate 45 degrees, promoting more flexible σ bonds in the system.

Summary: Molecular dynamics simulation

Cr-based systems: *Observed possible impurity gettering*

- N diffused from inside the matrix to the interfacial boundary
- Charge distribution and DOS properties indicate improved ductility
- Results in consistency with Brady's experimental work:

“impurity management effects”

Brady, et.al. Mat. Sci. & Eng. A, 358, 243 (2003)

Mo-based systems: *No impurity gettering observed*

- O impurity stable in matrix after 1.6 ps (1600 steps)
- Significant relaxation in the spinel phase due to lattice mismatch
- Results support Schneibel's conclusion

“grain size optimization effects”

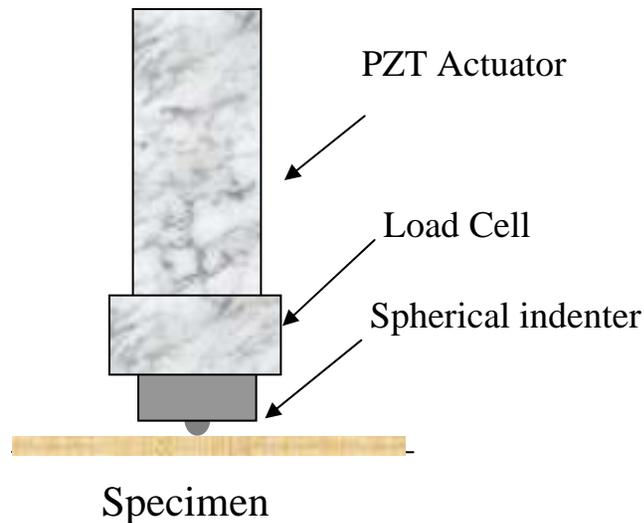
Schneibel, et.al. Metall. & Mater. Trans. 34A, 25 (2003)

Task 2: In-situ mechanical property measurement

Outline

- Micro-indentation Technique Development
 - Gen I: Transparent Indenter Measurement (TIM) Technique
 - Gen II: Simplified TIM Technique
 - **Gen III**: Multi-partial unloading indentation technique
 - **Capability**: Young's modulus, hardness, stress-strain curve of alloys or thin-film coating, surface stiffness response measurement of multi- layers structures
- Ductile/Brittle assessment using indentation technique
 - Indentation-induced surface cracking
 - Surface profile/slip lines/shear bands

Gen III: Multi-Partial Unloading Indentation Technique (A Load-Based Algorithm)

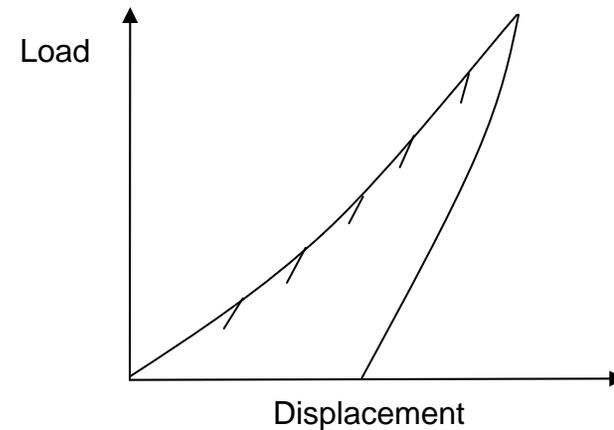


Load-depth sensing indentation system
without imaging

Governing Equations

$$\frac{dh}{dp} = C \times \frac{1}{p^{1/3}} + C_s$$

$$C = (6RE_r^2)^{-1/3}$$



Multi-partial unloading indentation technique

Applications:

- Young's modulus
- Stress-strain curve
- Indentation creep, fatigue

Potential:

Portable Indentation System

Gen III: Multi-Partial Unloading Indentation Technique

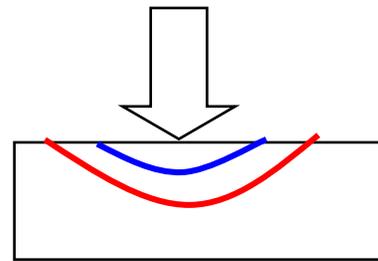
$$\left. \begin{aligned} \frac{dh}{dp} \Big|_1 &= C \times \frac{1}{p_1^{1/3}} + C_s \\ \frac{dh}{dp} \Big|_2 &= C \times \frac{1}{p_2^{1/3}} + C_s \end{aligned} \right\}$$

Double-partial unloading

$$\frac{dh}{dP} \Big|_1 - \frac{dh}{dP} \Big|_2 = C \times \left(\frac{1}{p_1^{1/3}} - \frac{1}{p_2^{1/3}} \right)$$

Multiple-partial unloading

$$\left(\frac{dh}{dp} \right) = C \times \left(\frac{1}{p^{1/3}} \right) + C_s$$



$$y = ax + b$$

$$x = \frac{1}{p^{1/3}}$$

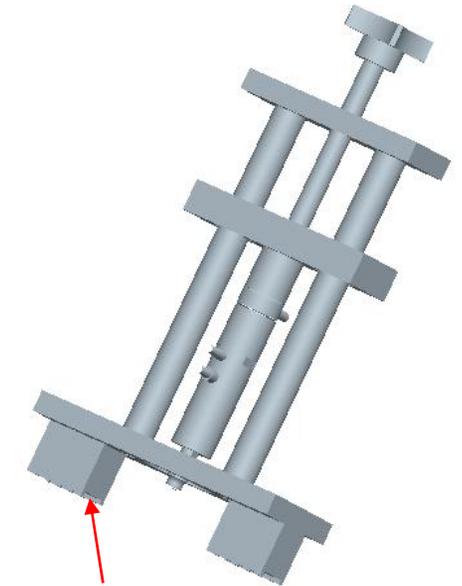
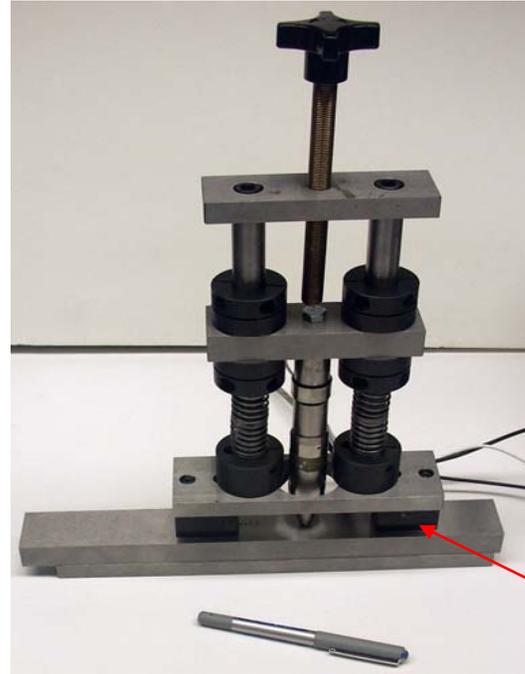
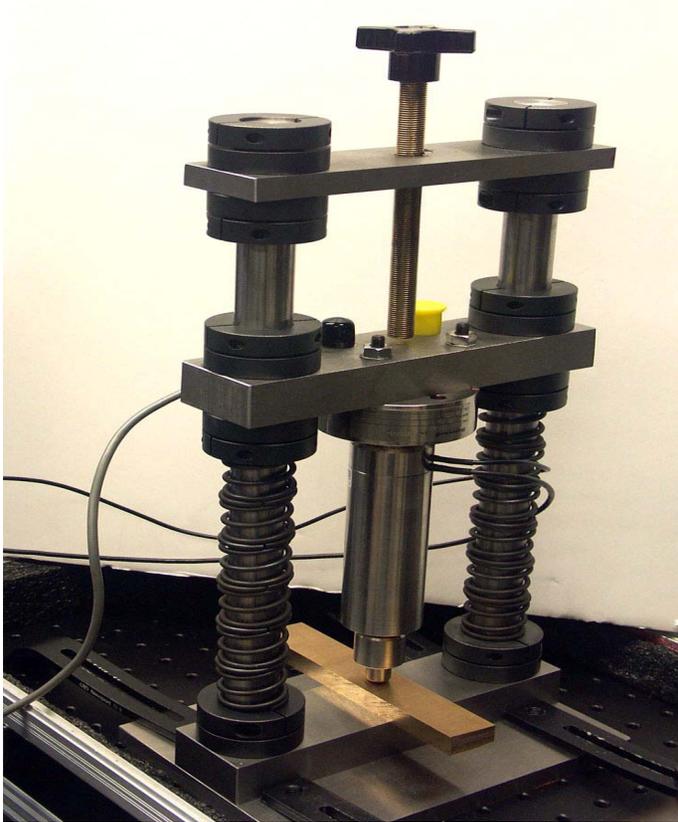
$$y = \frac{dh}{dp}$$

$$a = C = \left(6RE_r^2 \right)^{-1/3}$$

$$b = C_s$$

$$E = \frac{1 - \nu^2}{\frac{1}{E_r} - \frac{1 - \nu_0^2}{E_0}}$$

Table-Top Micro-Indentation Unit Portable Micro-Indentation Unit



Electromagnet Mount

Software for both units



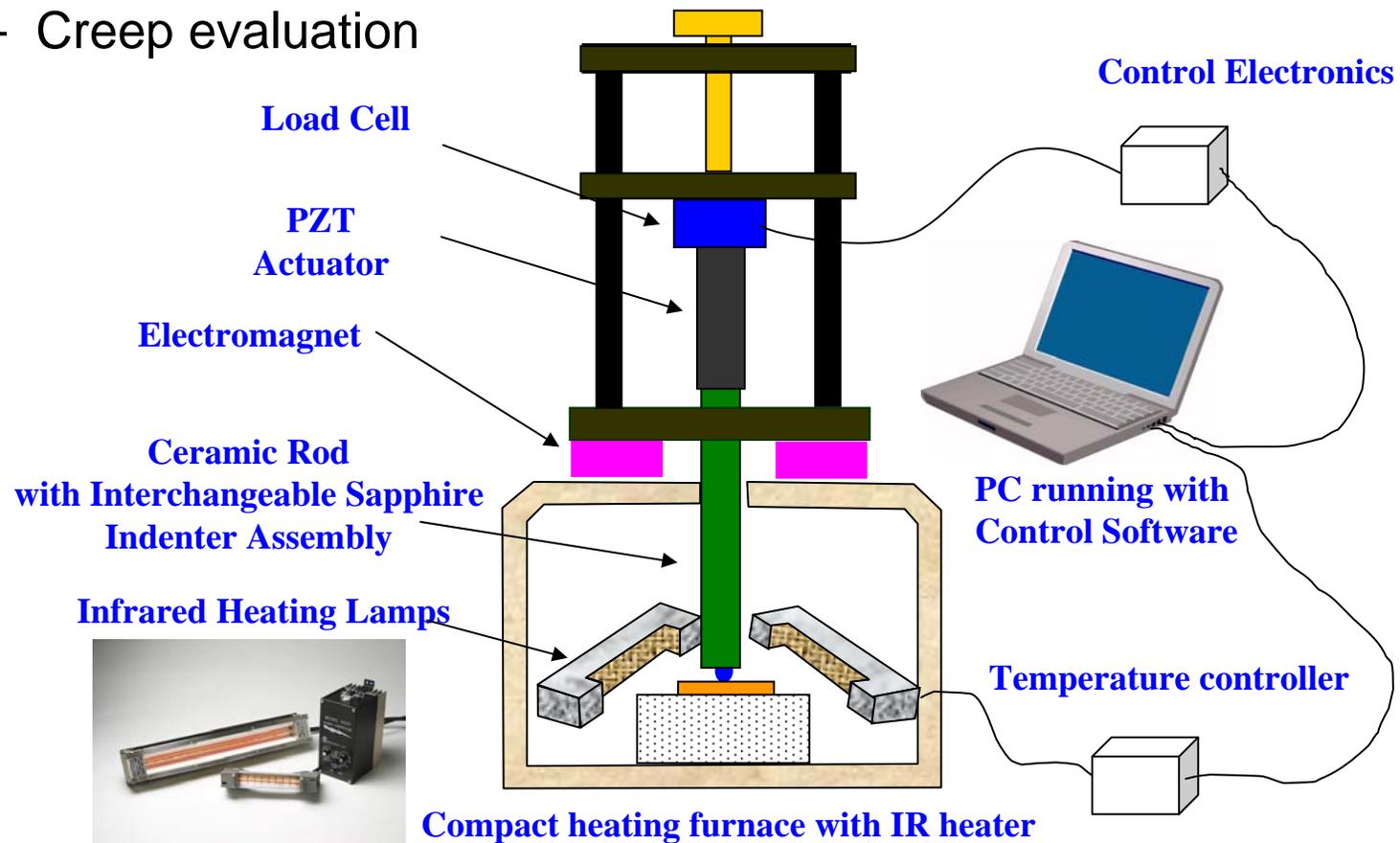
Validation: Portable Micro-Indentation Unit

Typical Results

<i>Test</i>	<i>Bronze 932</i>	<i>Aluminum 6061</i>	<i>01 Tool Steel</i>
<i>Number</i>	<i>GPa</i>	<i>GPa</i>	<i>GPa</i>
Book Value	103 -124	68 - 71	190 - 210
1	109.98	68.23	207.92
2	113.74	68.57	209.78
3	113.98	68.14	210.01
4	109.90	68.43	204.75
5	111.99	70.51	211.66
6	115.45	69.07	209.78
7	119.02	68.40	210.48
8	114.06	77.15	212.37
9	121.97	73.40	215.03
10	124.38	67.77	199.94
Average	115.45	69.97	209.17
Standard Deviation	4.88	3.03	4.22

Work in Progress

- High Temperature Indentation
 - Degradation evaluation using multi-partial unloading indentation technique
 - Creep evaluation



Materials Matrix

(Alloys received from M.P. Brady and J. H. Schneibel, ORNL)

#678, Mo-3.4wt%MgAl₂O₄ : 1800°C/4hr/3ksi/Vacuum, Mo powder 2-8μm, MgAl₂O₄, 1-5μm

#696, Mo-3.0wt%MgAl₂O₄ : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8μm, MgAl₂O₄, 1-5μm

#695, Mo only : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8μm

#697, Mo-6.0wt%MgAl₂O₄ : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8μm, MgAl₂O₄, 1-5μm

#698, Mo-3wt%MgO : 1800°C/1hr/3ksi/Vacuum, Mo powder 2-8μm, MgO, 1-5μm

Cast Re-(26-30) Cr wt% nominal

(Powder mix prepared at WVU using Ultrasound Mixing Technique and sent to ORNL for vacuum hot-pressed)

Mo-5.0wt%MgAl₂O₄ : 1800°C/0.5hr/3ksi/Vacuum

Mo-5wt%MgO : 1800°C/1.0hr/3ksi/Vacuum

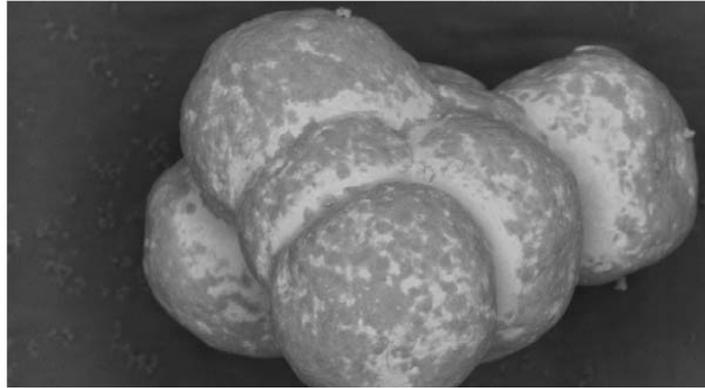
Mo-5.0wt%TiO₂ : 1700°C/0.5hr/3ksi/Vacuum

(Powder mix prepared using Hosakawa Mechano Chemical Bonding processing technique from Hosokawa, then vacuum hot-pressed)

Mo-2.5wt%MgAl₂O₄ (Before MCB process): 1800°C/0.5hr/3ksi/Vacuum

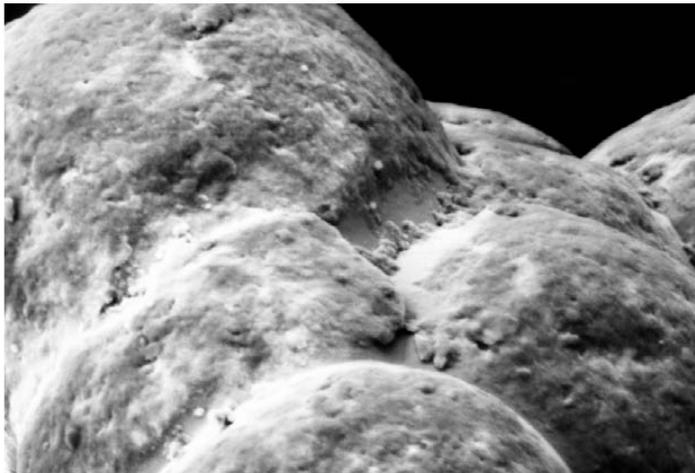
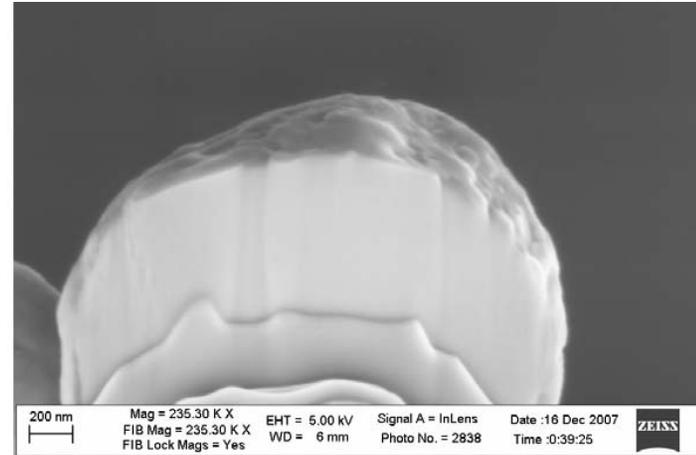


Mechano Chemical Bonding & Particle Design

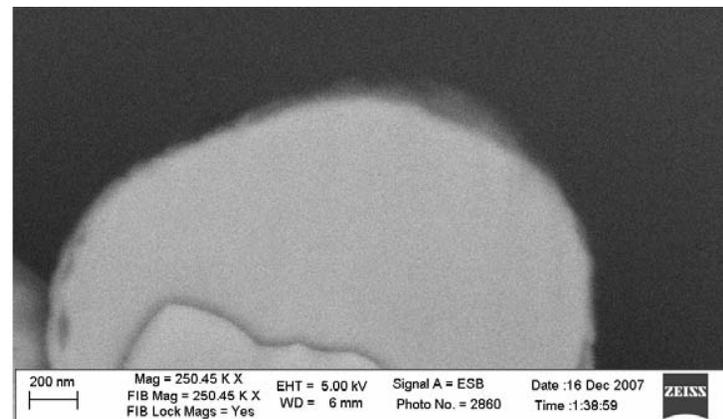


Mo particle covered with Nano-MgAl₂O₄ particles, brighter region has less MgAl₂O₄ covered

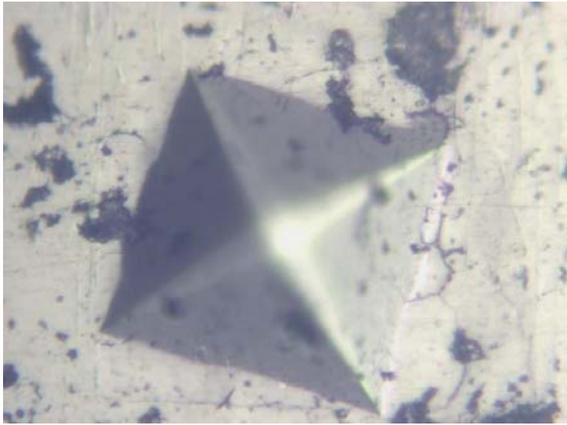
SEM image (Inlens detector) Mo particle is cut by FIB



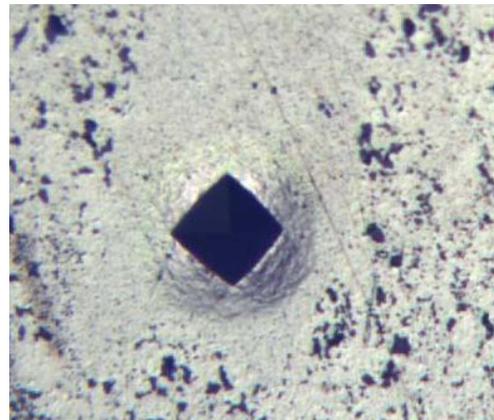
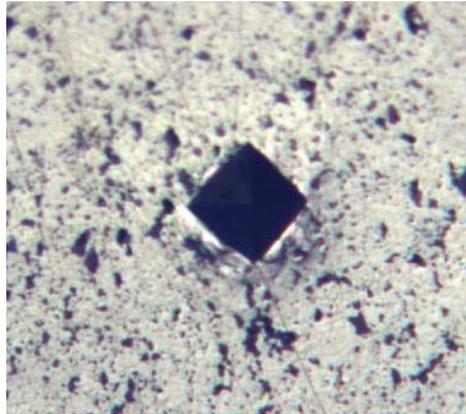
ESB image: bright areas are Mo and less bright cover is AlMgO



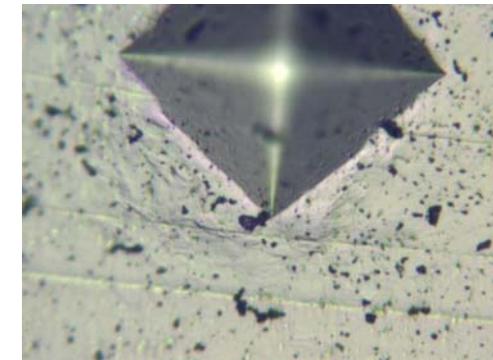
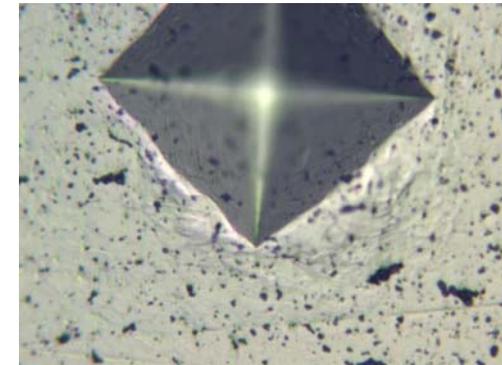
Comparison of Ductility through Vickers Indentation



#697: Cracks observed, and no sign of ductility improvement



Mo-Nano MgAl₂O₄ with sonication process (WVU), Cracks observed in the first, and some region showed ductility



Mo-Nano MgAl₂O₄ with MCB process (WVU), Cracks were not observed, and many observed ductility

Summary: Young's Modulus Measurement

Material	Young's modulus (GPa)
Cast Re-(26-30) Cr wt%	234
#678, Mo-3.4wt%MgAl ₂ O ₄	229
#696, Mo-3.0wt%MgAl ₂ O ₄	200
#697, Mo-6.0wt%MgAl ₂ O ₄	192 (Tensile test : 189)
#698, Mo-3wt%MgO	211
Mo-MgO (WVU)	254
Mo-MgAl ₂ O ₄ (WVU)	202
Mo-TiO ₂ (WVU)	226

(Averaged value from five indentation tests, typical)

Conclusion:

Task 1: Atomistic Modeling

- Identified *microscopic* criteria to predict **brittle/ductile** properties. *These criteria can explain the mechanisms and be used in larger scale simulations to optimize performance*
- Observed possible tendency for **impurity gettering**. *This work demonstrates the capability of studying the dynamic effects and carrying out large scale simulations*

Task 2: In-situ Mechanical Property Measurement

- Developed a **micro-indentation technique** for **in-situ mechanical property** measurement.
- A new powder mixing processing technique has been successfully applied to coat a thin layer of metal oxides on Mo particles. The **Mechano-Chemical Bonding (MCB)** process can **bond nano-size particles** onto the surfaces of larger host particles to achieve desirable **uniform dispersing of the nano-sizes oxides in the alloy matrix**. Preliminary results show evidences of using the MCB processing technique to produce cost-effective Mo alloys with improved room-temperature ductility.