# BASIC MECHANISMS INVOLVED IN FAST SINTERING

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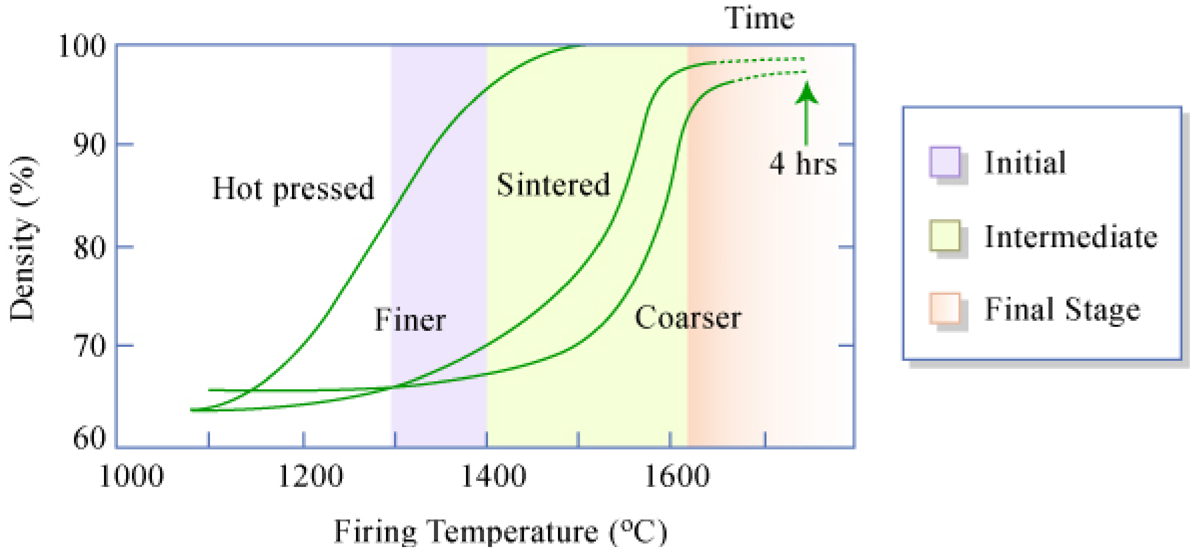
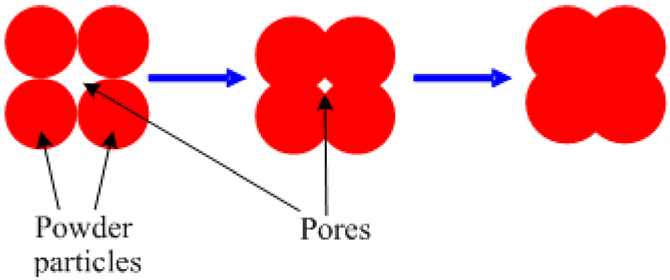
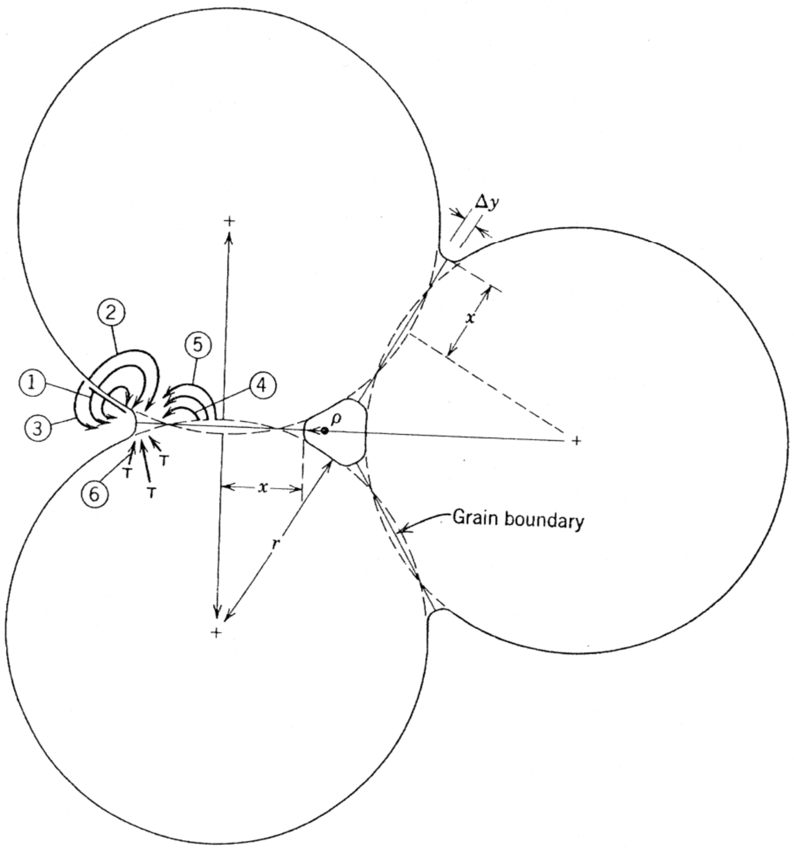
## Sintering requires mass transfer through diffusion




The mechanism of mass transfer depends on the material, the experimental conditions, and the sintering stage

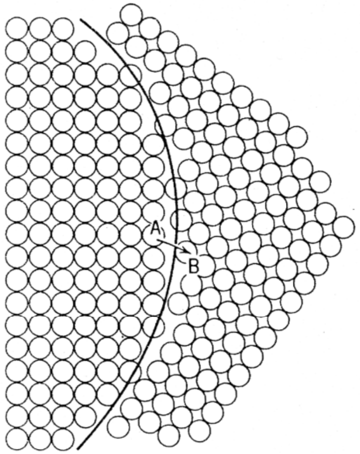
# MECHANISMS OF SINTERING

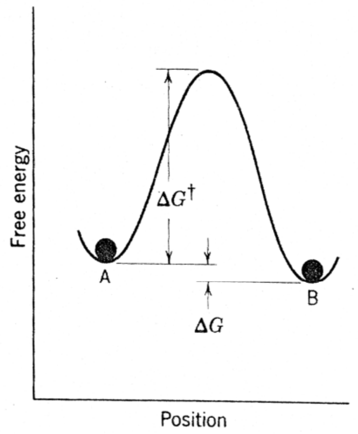


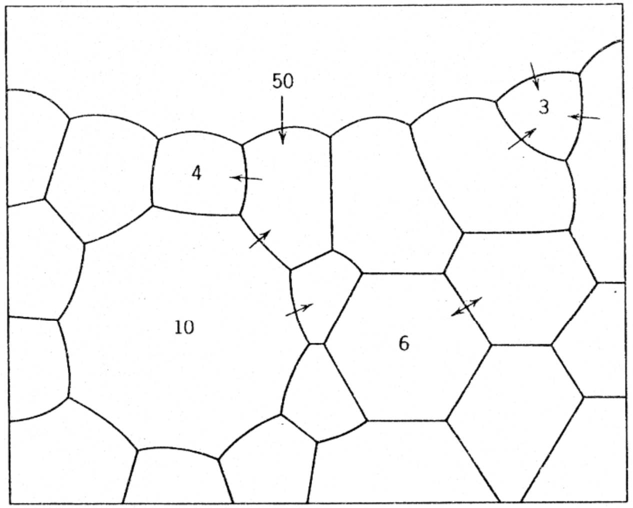

| Mechanism Number | Transport Path | Source of Matter | Sink of Matter |
|---|---|---|---|
| 1 | Surface diffusion | Surface | Neck |
| 2 | Lattice diffusion | Surface | Neck |
| 3 | Vapor transport | Surface | Neck |
| 4 | Boundary diffusion | Grain boundary | Neck |
| 5 | Lattice diffusion | Grain boundary | Neck |
| 6 | Lattice diffusion | Dislocations | Neck |

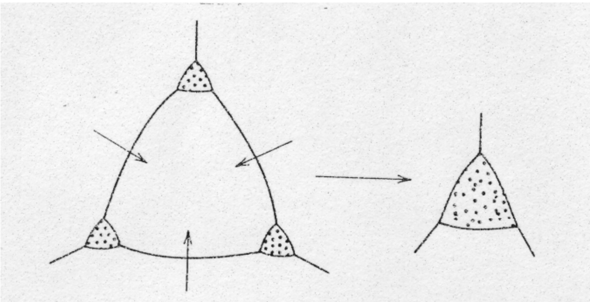
W.D.Kingery, H.K.Bowen, D.R.Uhlmann, Introduction to ceramics , Wiley

## MECHANISMS OF SINTERING



W.D.Kingery, H.K.Bowen, D.R.Uhlmann, Introduction to ceramics , Wiley

# MECHANISMS IN FAST SINTERING

• FAST sintering involves experimental conditions more complex than in traditional sintering, so **more** mass transfer mechanisms might be involved

• The number of involved mechanisms and their relative relevance is still being debated

• It is very dependent on the material physical and chemical properties and on the experimental conditions

# MECHANISMS IN FAST SINTERING

- Arc and spark discharge
- Electromigration
- Electric field induced diffusion
- Temperature gradients
- Pressure and stress gradient
- Modification of defects concentration
- Heating rate

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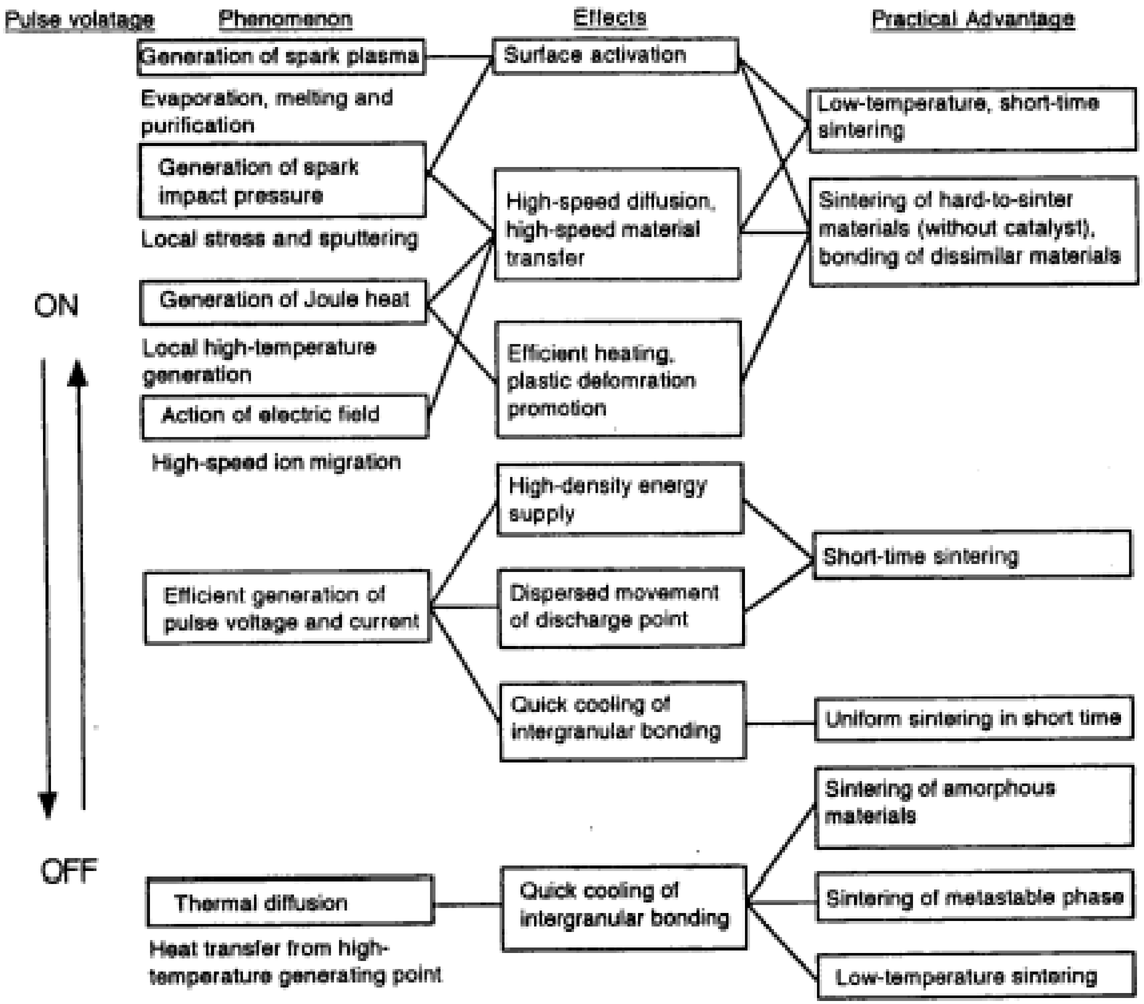
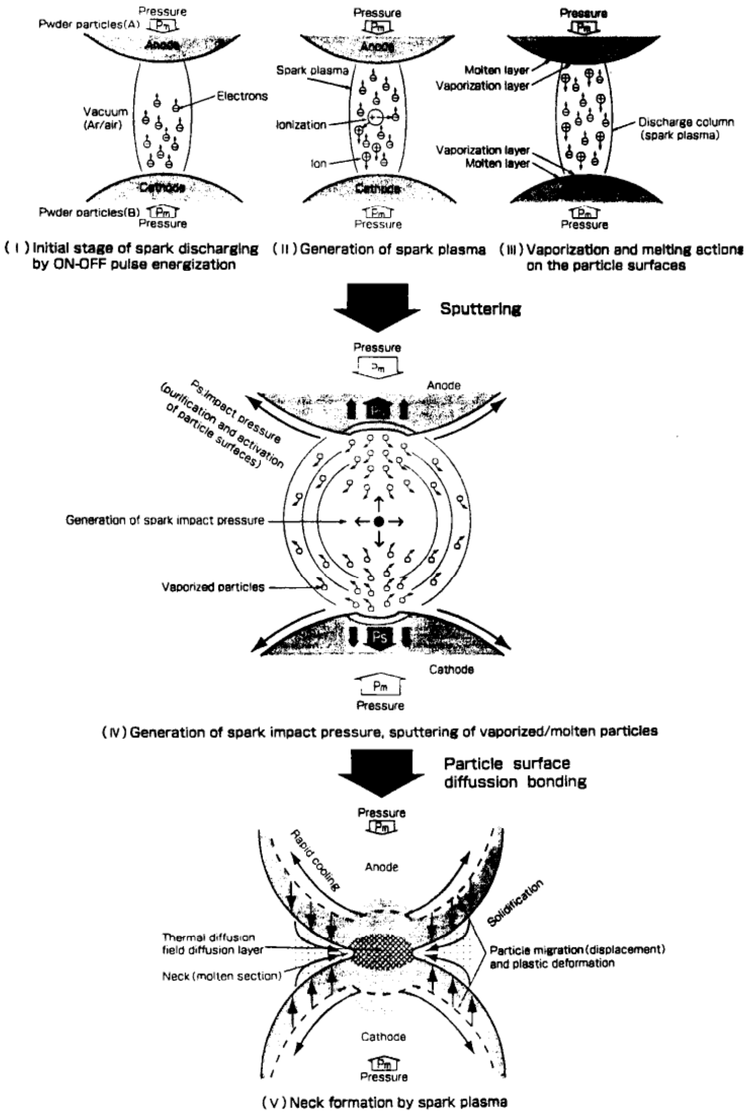
# MECHANISMS IN FAST SINTERING




M.Tokita, Proc. NEDO Int. Symp. Functionally Graded Materials, Kyoto, Japan, 1999

# ARC AND SPARK DISCHARGE




M.Tokita, Proc. NEDO Int. Symp. Functionally Graded Materials, Kyoto, Japan, 1999

# ARC AND SPARK DISCHARGE

• **Arc discharge**

high current (>10 A) and low voltage (< 20 V)

•**Spark discharge**

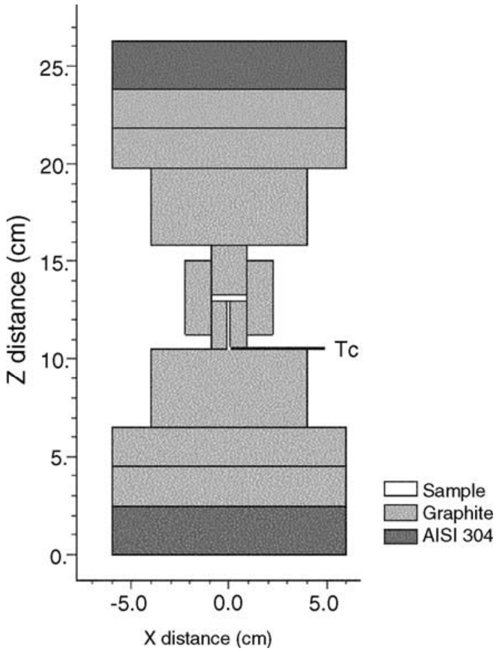
transient very high current (kA) and voltage (kV/cm)

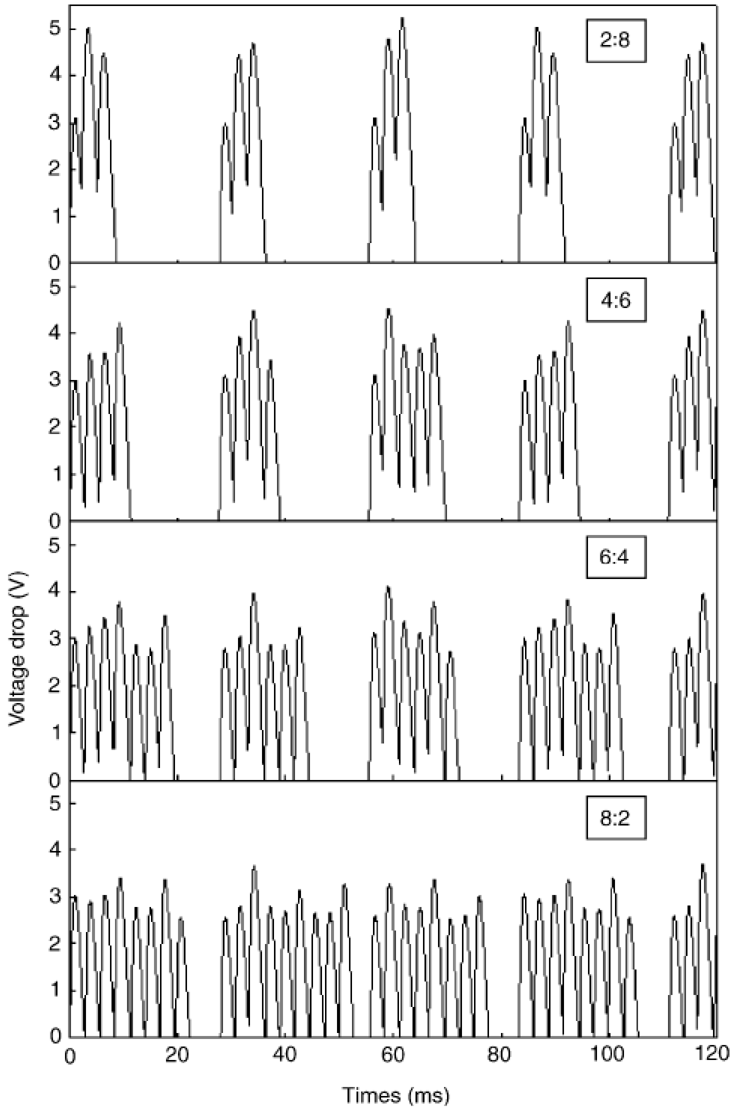
•**Glow discharge**

low current (< 1A) and relatively high voltage (300 V)

# ARC AND SPARK DISCHARGE

**What is the voltage that the sample experience in a FAST apparatus?**

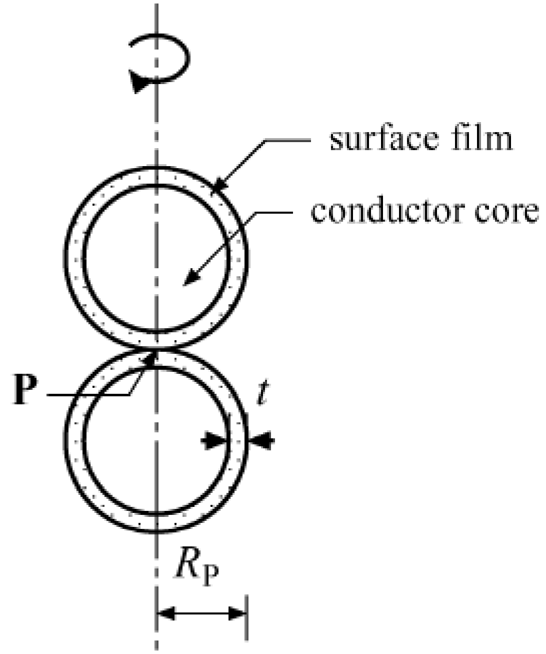


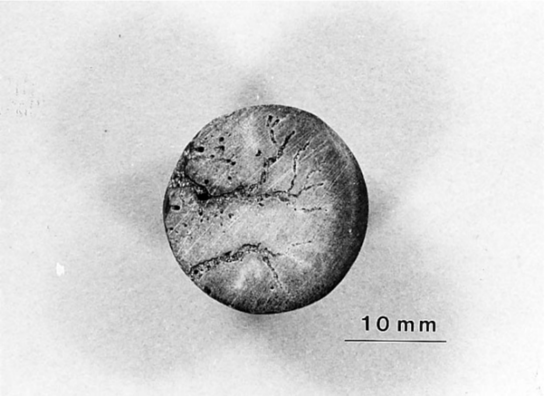

U. Anselmi-Tamburini, S. Gennari, J.E. Garay, Z.A. Munir, Mat. Sci. Eng. A 394 (2005) 139–148

# ARC AND SPARK DISCHARGE

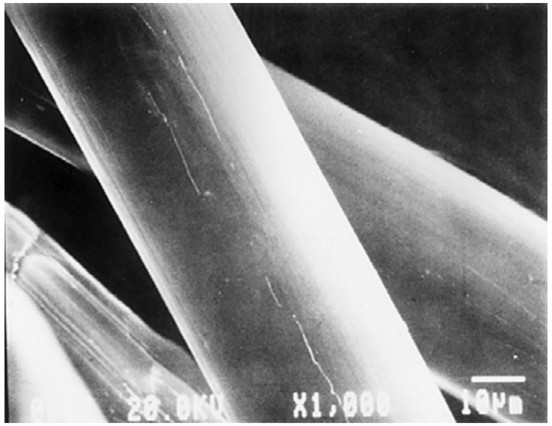
The imposed fields are just few volts, but polarization effects can produce localized fields order of magnitude higher



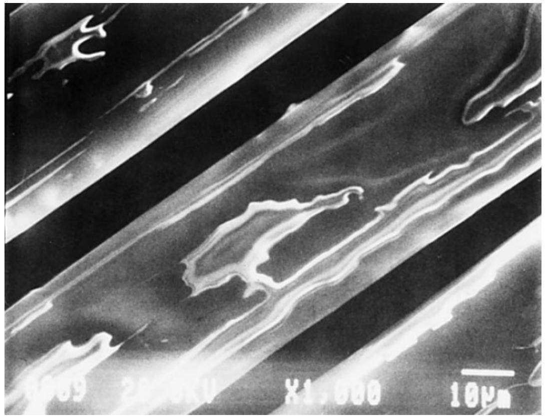
## Evidences supporting the presence of discarges




Electric discharge pattern on the surface of CeSiNO2.



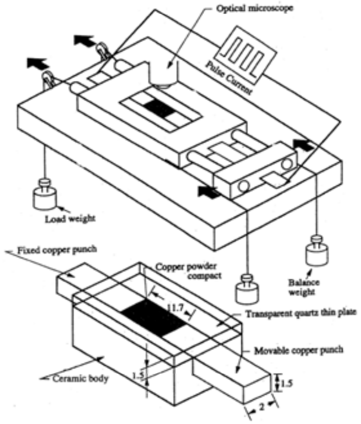

SEM image of polyethylene fiber.

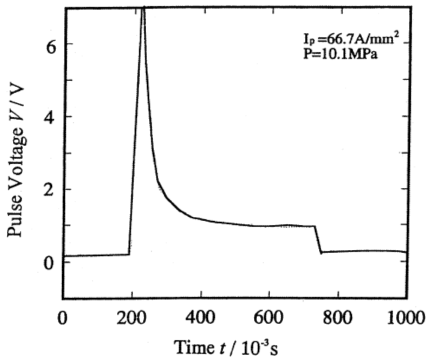


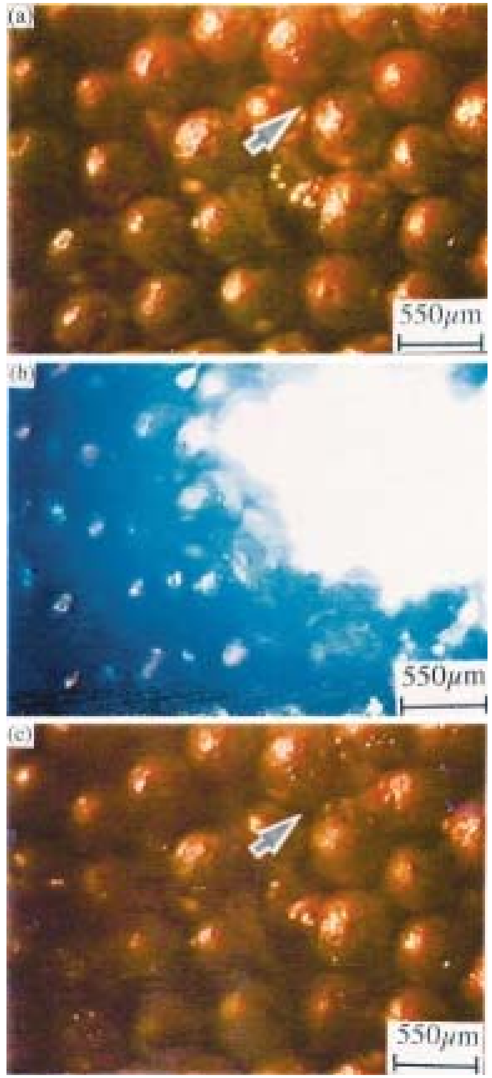

SEM image of the polyethylene fiber exposed to electrical discharge in air.

M. Omori : Materials Science and Engineering A287 (2000) 183–188

## Evidences supporting the presence of discarges



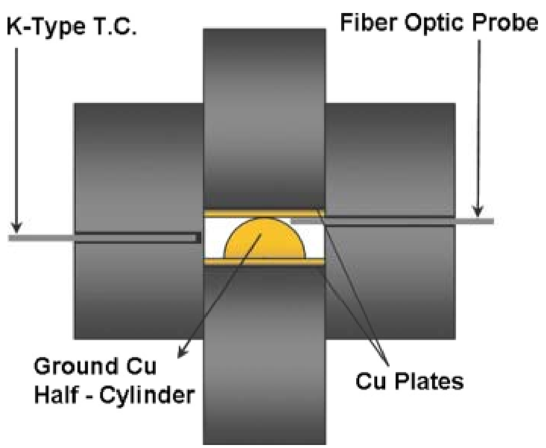



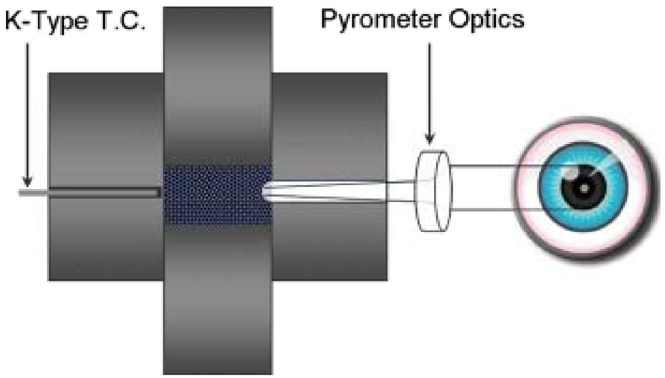



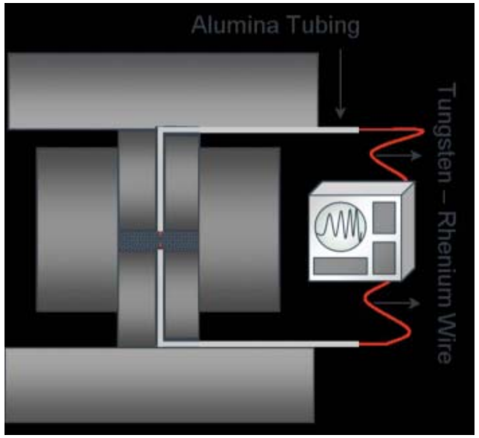

O. Yanagisawa et al. / Materials Science and Engineering A350 (2003) 184/189

# ARC AND SPARK DISCHARGE

## Evidences against the presence of discarges



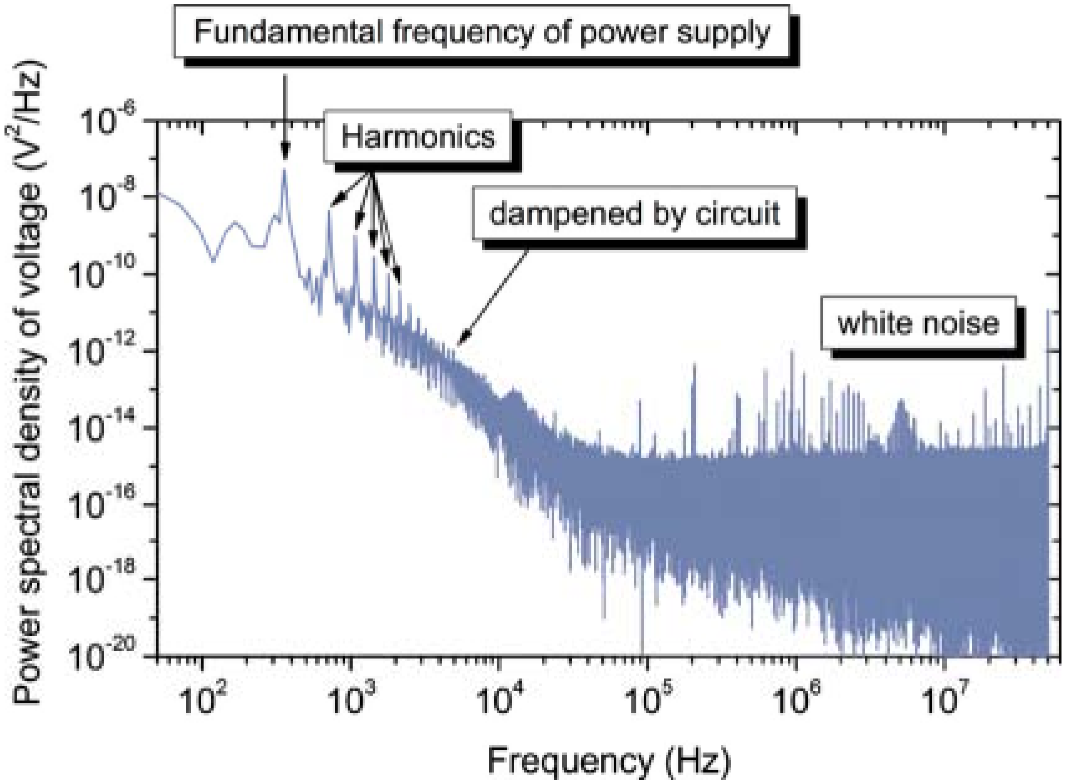




D.M. Hulbert, A. Anders, D. V. Dudina, J. Andersson, D. Jiang, C. Unuvar, U. Anselmi-Tamburini, E. J. Lavernia, and A.K. Mukherjee, J. Appl. Phys. 104 (2008) 033305

# ARC AND SPARK DISCHARGE

## Evidences against the presence of discarges




A FFT plot of one duty cycle of the SPS process. This plot is for the SPS of 325 mesh 99.9% pure Al powder after a temperature of 100 °C was reached using a heating rate of 100 °C/min.

D.M. Hulbert, A. Anders, D. V. Dudina, J. Andersson, D. Jiang, C. Unuvar, U. Anselmi-Tamburini, E. J. Lavernia, and A.K. Mukherjee, J. Appl. Phys. 104 (2008) 033305

# MECHANISMS IN FAST SINTERING

- Arc and spark discharge
- **Electromigration**
- Electric field induced diffusion
- Temperature gradients
- **Pressure and stress gradient**
- Modification of defects concentration
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# DIFFUSION AND EXTERNAL DRIVING FORCES

$$J = -D\frac{\partial C}{\partial x} + \boxed{\tilde{v}C}$$

$$\tilde{v} = uF$$

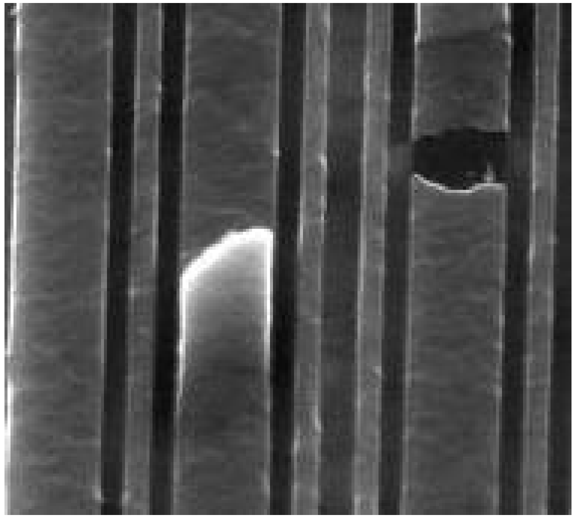
*u* is the mobility
*F* the driving force

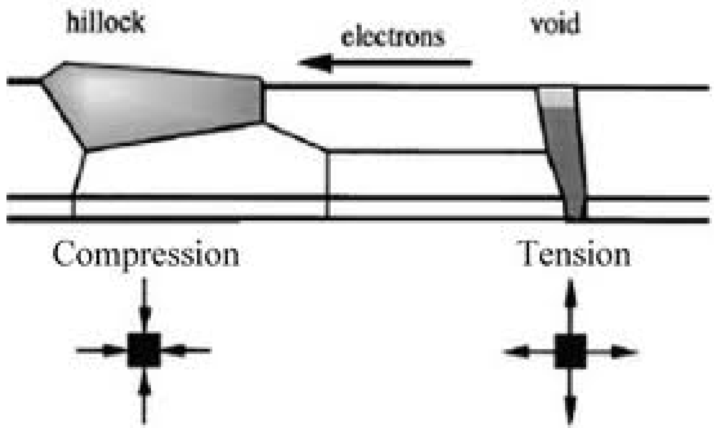
| Force | Expression | Remarks |
|---|---|---|
| Gradient of electrical potential $\boldsymbol{E} = -\boldsymbol{\nabla} U$ | $q^* \boldsymbol{E}$ | $q^*$: effective electric charge |
| Gradient of chemical potential (non-ideal part) | $-\boldsymbol{\nabla}\mu$ | $\mu$: chemical potential |
| Temperature gradient $\boldsymbol{\nabla} T$ | $-(Q^*/T)\boldsymbol{\nabla} T$ or $-S\nabla T$ | $Q^*$: heat of transport<br>$S$: Soret coefficient |
| Stress gradient | $-\boldsymbol{\nabla} U_{el}$ | $U_{el}$: elastic interaction energy due to stress field |

H.Mehrer , Diffusion in solids, Springer

# ELECTROMIGRATION

- Correlation between ionic and electronic conduction.
- Usually observed in metals for current densities > 1000 A/cm$^2$
- Huge importance in semiconductor industry





# ELECTROMIGRATION

$$J = -D\frac{\partial C}{\partial x} + uFC$$

For electromigration:

$$F = |e|Z^{*}E$$
$$= |e|\left(Z^{e} + Z^{w}\right)E$$

$Z^e$ electrostatic interaction
$Z^w$ "wind effect"

If the mobility is given by the Nernst-Einstein equation : $u = \dfrac{D}{kT}$

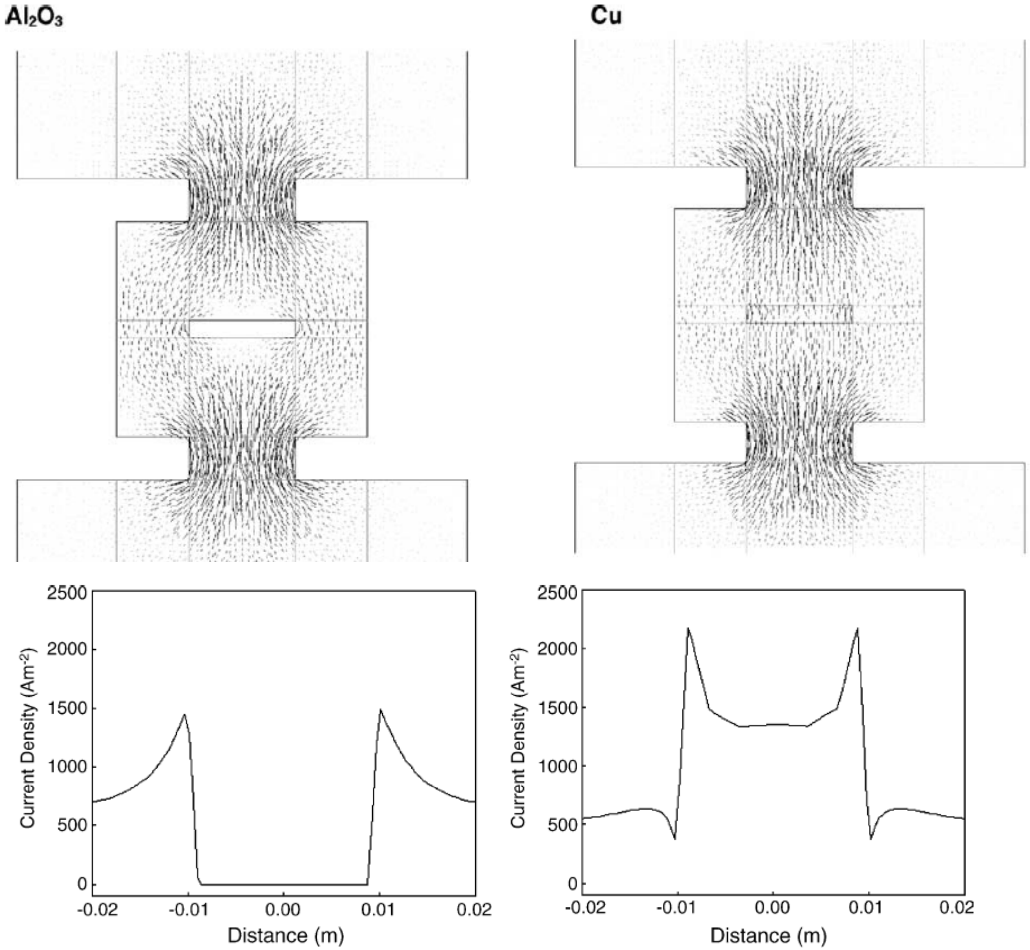
$$J = -D\frac{\partial C}{\partial x} + \frac{DC}{kt}Z^{*}|e|E$$
$$= -D\frac{\partial C}{\partial x} + \frac{DC}{kt}Z^{*}|e|\rho j$$

Vacancy diffusion in metals

D.G. Pierce and P. G. Brusius,, *Microelectron. Reliab., Vol. 37, No. 7, pp. 1053 -1072, 1997*

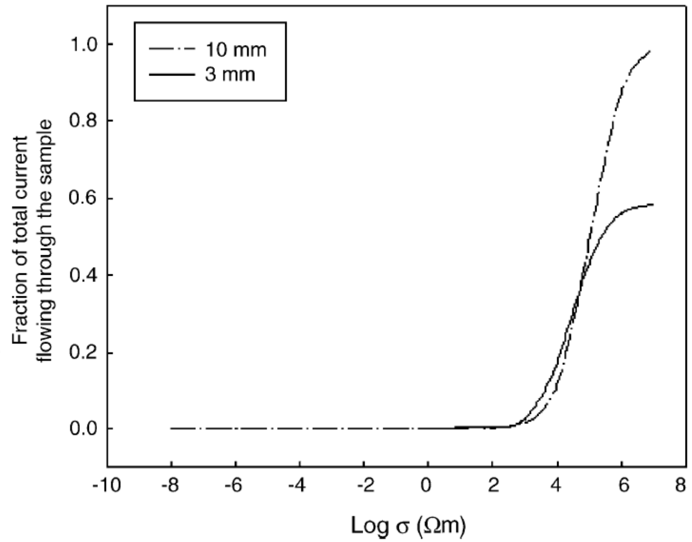
# ELECTROMIGRATION

## How much current flows through the sample in a FAST system?




(a) Alumina

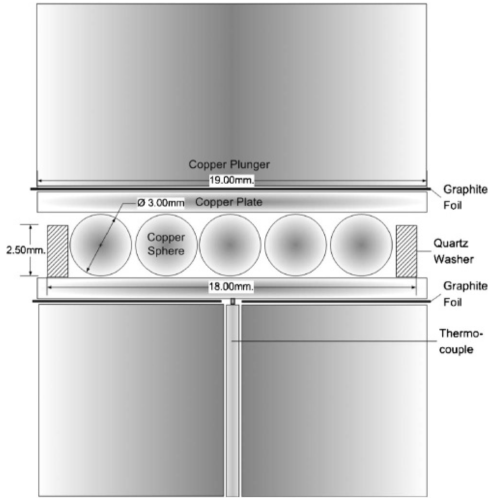
(b) Copper



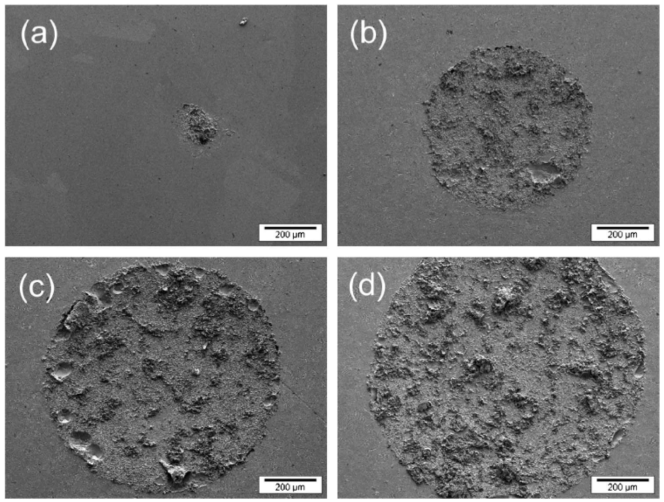

U. Anselmi-Tamburini, S. Gennari, J.E. Garay, Z.A. Munir, Materials Science and Engineering A 394 (2005) 139–148

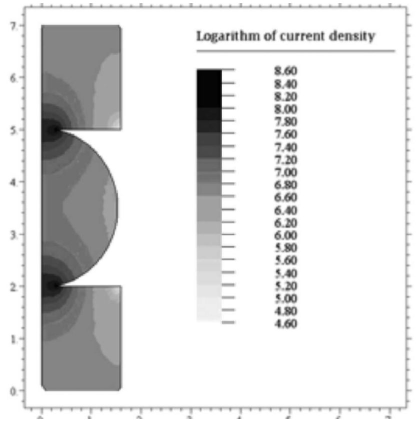
# ELECTROMIGRATION AND SINTERING

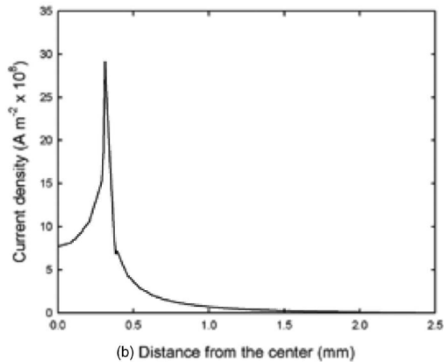
Copper spheres on Copper plate

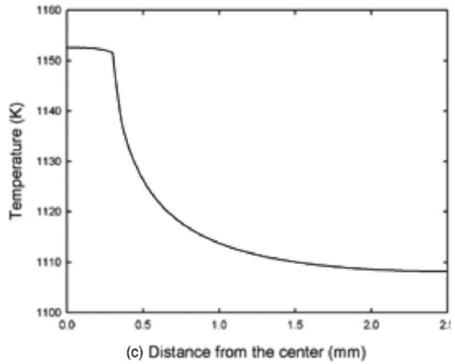



900 °C
60 min
a) 0 A
b) 700 A
c) 850 A
d) 1040 A.




J.M. Frei, U.Anselmi-Tamburini, Z.A. Munir, J. Appl. Phys. 101 (2007) 114914

# ELECTROMIGRATION AND GRAIN BOUNDARIES

$$J_l = \frac{1}{kT} N_l D_l j\rho e Z_l^*$$

$$J_b = \frac{1}{kT} \frac{N_b \delta}{d} j\rho e Z_b^*$$

$\delta$ boundary width
$d$ grain size

$$\frac{J_l}{J_b} = \frac{N_l}{N_b} \frac{\delta}{d} \frac{D_l}{D_b} \frac{Z_l^*}{Z_b^*} j\rho e$$

$Z_l^*$ and $Z_b^*$ do not differ by more than an order of magnitude, so for Al with *d=1$\mu$m and 0.5* $T_m$:

$$\frac{N_l}{N_b} \cong 1 \quad \frac{\delta}{d} \cong 10^3 \quad \frac{D_l}{D_b} \cong 10^{-7} \quad \frac{J_l}{J_b} \cong 10^{-4}$$

P.S.Ho and T.Kwok, Rep.Prog.Phys., 52 (1989) 301

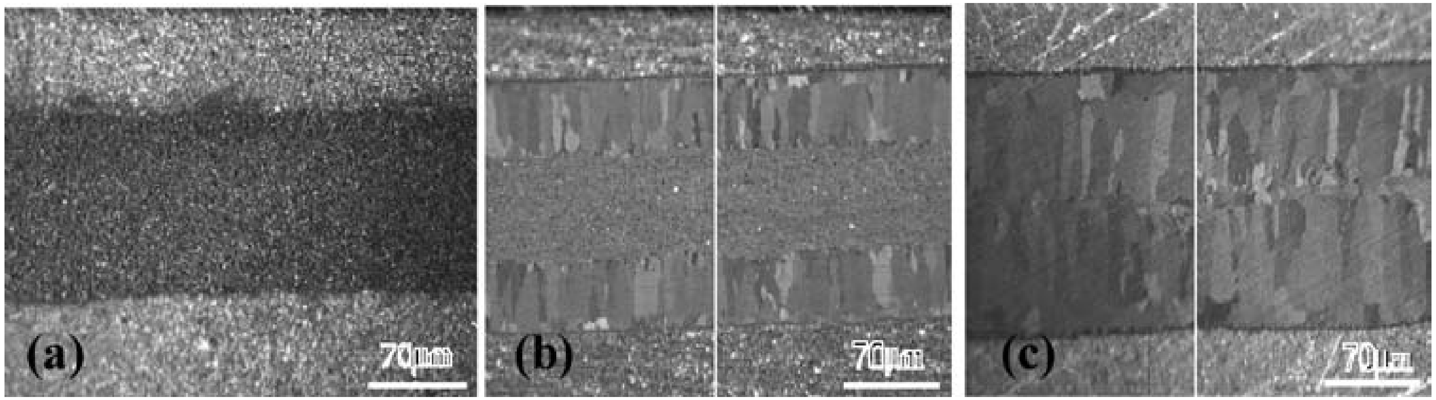
# ELECTROMIGRATION AND REACTIVITY

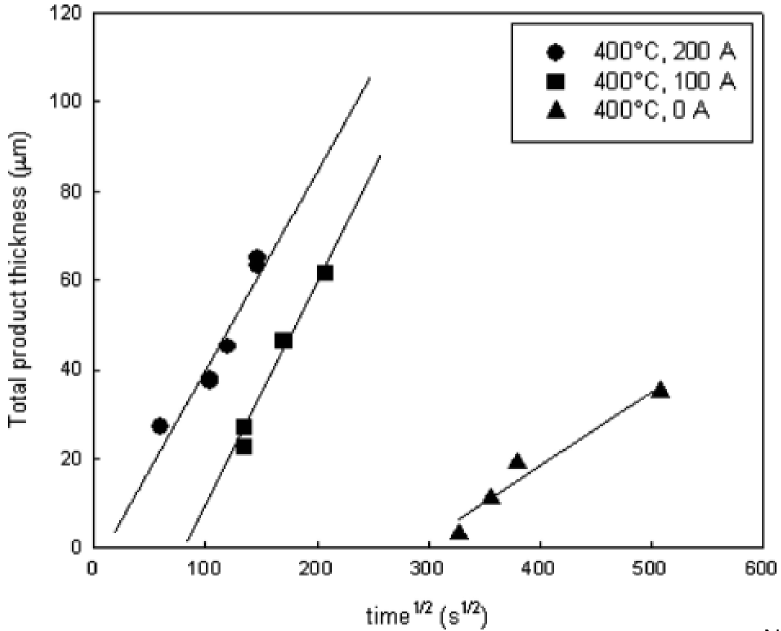
## Formation of intermetallic compounds

Al

Au

Al



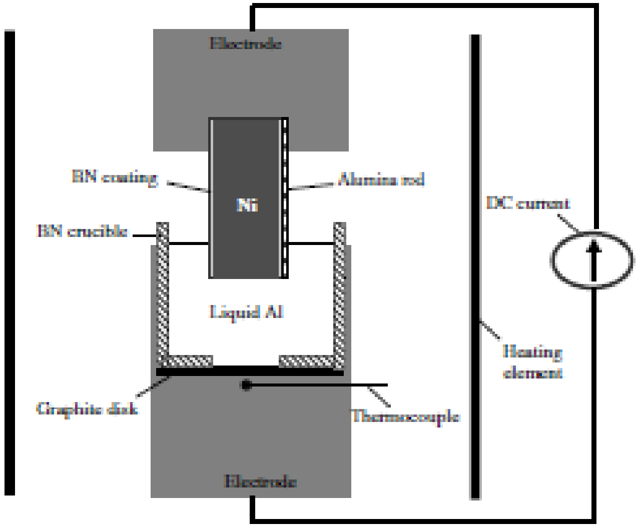

The enhancement depends on the intrinsic diffusivity and on the magnitude of the electromigration on the various species

A general phenomenologial model has been developed by C.-M. Hsu, D. S.-H. Wong, S.-W-Chen, J.Appl.Phys., 102 (2007) 023715

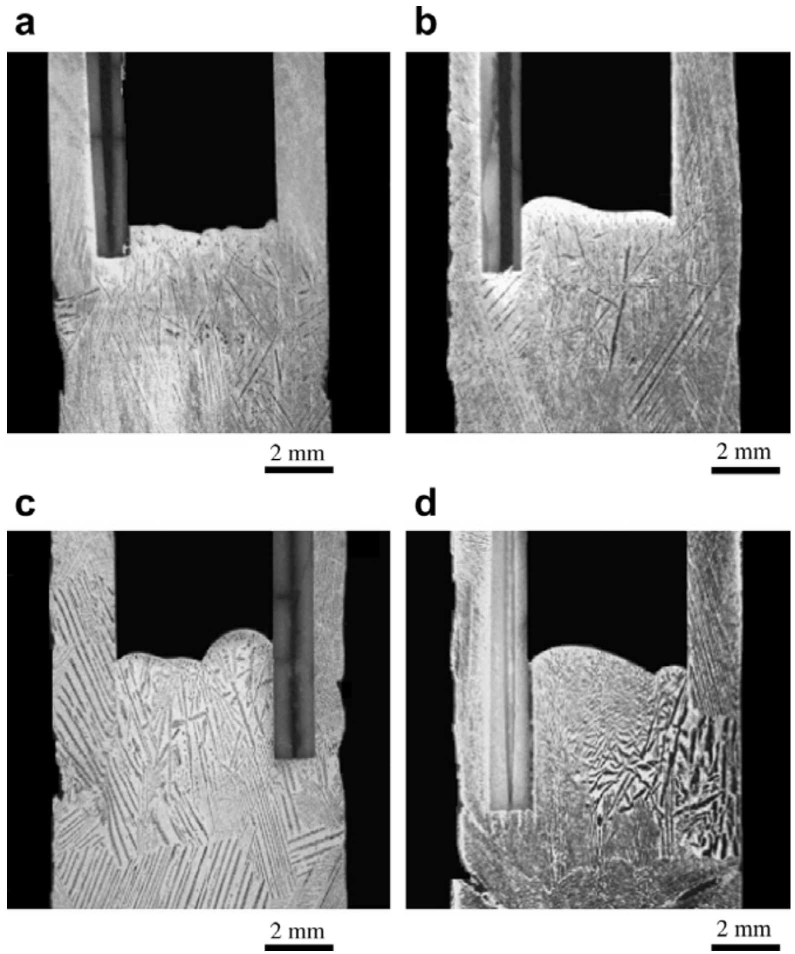
N.Bertolino, J.Garay, U.Anselmi-Tamburini, Z.A.Munir, Phil.Mag.B, 82 (2002) 969

# ELECTROMIGRATION IN SOLID-LIQUID REACTIVITY

## Formation of intermetallic compounds




767°C , 15 min
(a) 0 A/cm$^2$
(b) 316 A/cm$^2$
(c) 474 A/cm$^2$
(d) 585 A/cm$^2$




J.F. Zhao, C. Unuvar, U. Anselmi-Tamburini, Z.A. Munir , Acta Materialia 55 (2007) 5592–5600

# MECHANISMS IN FAST SINTERING

- Arc and spark discharge
- Electromigration
- **Electric field induced diffusion**
- Temperature gradients
- Pressure and stress gradient
- Modification of defects concentration
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# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

Diffusion under the influence of an external driving force

$$J = -D\frac{\partial C}{\partial x} + \tilde{v}C \qquad \tilde{v} = uF$$

$u$ is the mobility
$F$ is the driving force

In a ionic crystal the electric field produce a flux of material

$$F = qE \qquad u = \frac{D}{kT}$$

$$j = \tilde{v}C = \frac{qCD}{kT}E$$

Material flux

$$j_e = q\, j = \frac{q^2 CD}{kT}E$$

Electric current

$$j_e = \sigma E \qquad \sigma = \frac{q^2 CD}{kT}$$

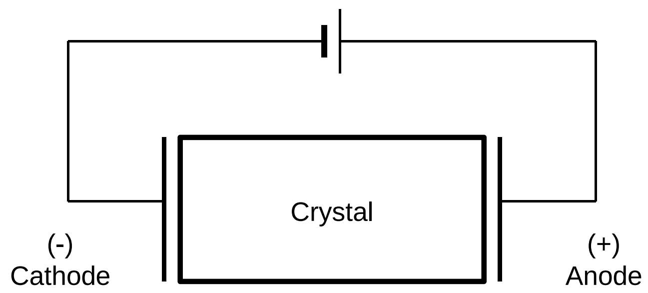
# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

- In ionic materials conduction is related to the defects concentration and mobility.
- Ionic and electronic defects concentrations are controlled by complex equilibria

- Purely ionic conductors
- Mixed conductors

**When ionic conduction is associated to trasfer of material there is the possibility of field induced sintering or densification**

# FIELD INDUCED DIFFUSION IN IONIC MATERIALS



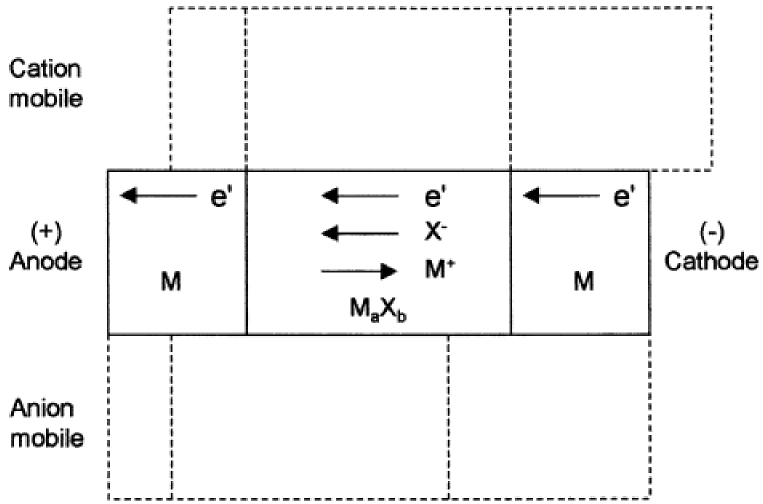

Four kind of electrodes

- Reversible to electrons and ions
- Semi-blocking ionic ( passing only ionic current)
- Semi-blocking electronic ( passing only electronic current)
- Blocking (passing neither ionic nor electronic currents) – *non contact field*

# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Mixed conductor – identical reversible electrodes

$$M(s) \rightarrow M^{|Z_1|(+)} + |Z_1|e'(M)$$

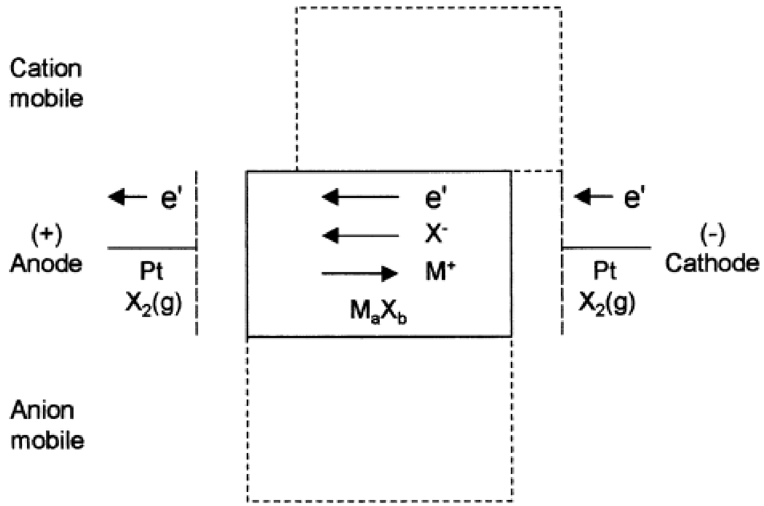



$$\frac{a}{b}M(s) + X^{|Z_2|(-)} \rightarrow \frac{1}{b}M_aX_b + |Z_2|e'(M)$$

S.C. Byeon, K.S. Hong, Mat.Sci.Eng., A287 (2000) 159-170

## Mixed conductor – reversible identical gas electrodes

$$\frac{1}{a}M_aX_b \rightarrow \frac{b}{2a}X_2(g)+M^{|Z_1|(+)}+|Z_1|e'(Pt)$$

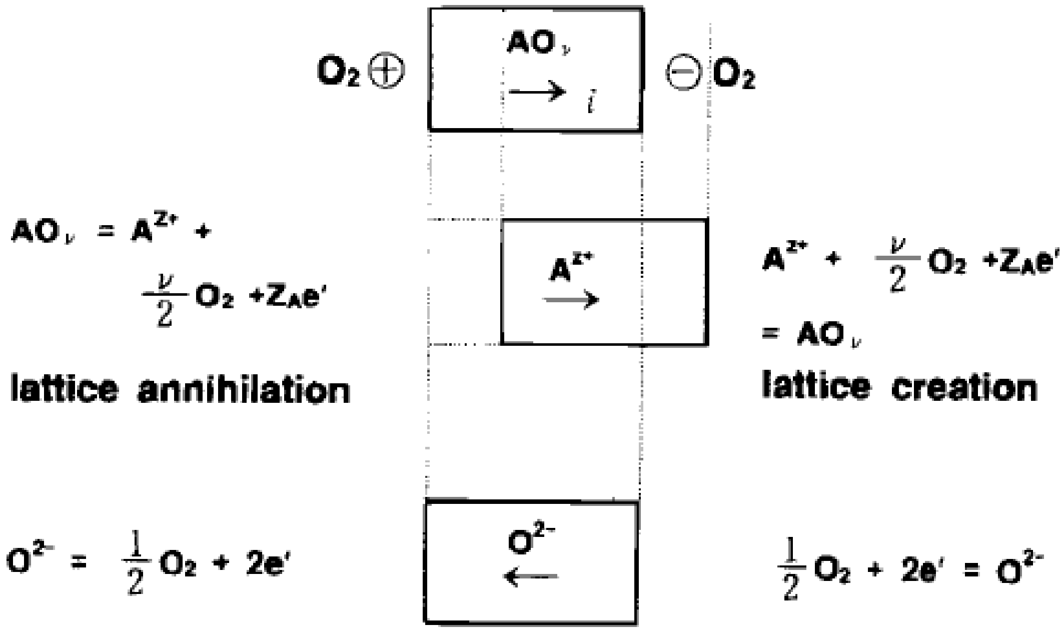



$$X^{|Z_2|(-)} \rightarrow \frac{1}{2}X_2(g)+|Z_2|e'(Pt)$$



S.C. Byeon, K.S. Hong, Mat.Sci. Eng., A287 (2000) 159-170

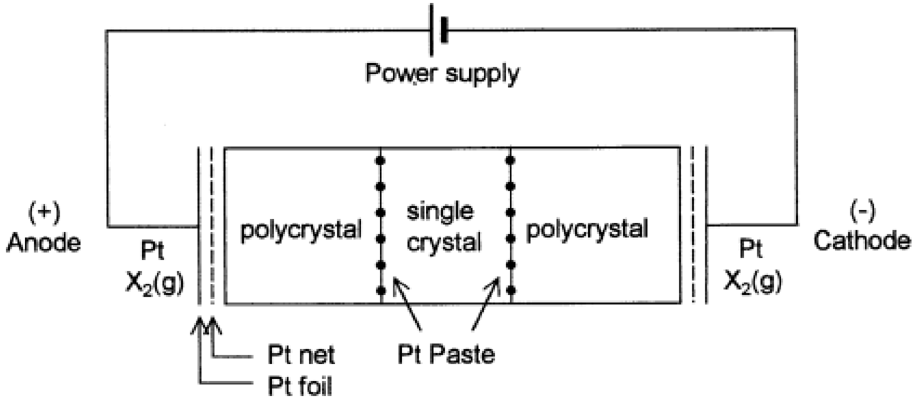
## Tubandt electrotransport experiment

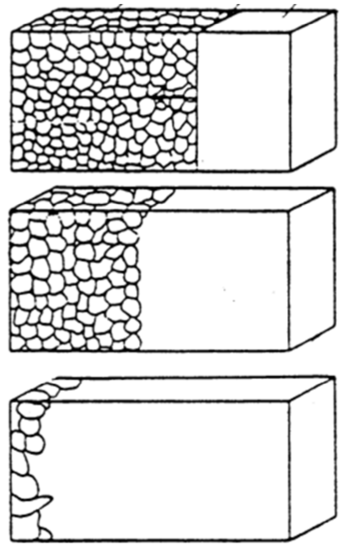


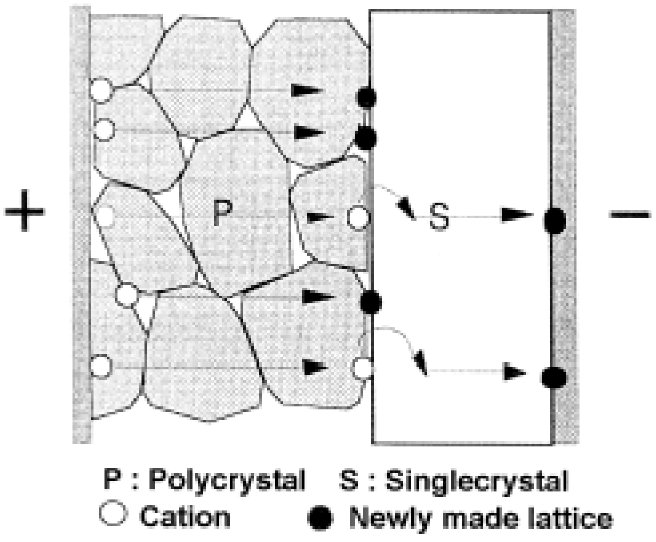

C.-S.Kim, H.-I.Yoo, J.Electrochem.Soc., 143 (1996) 2863

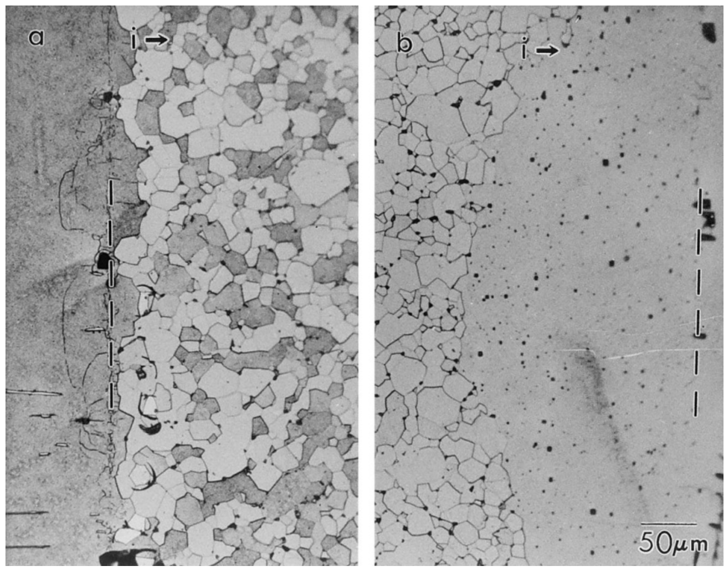
# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Electrotransport and sintering





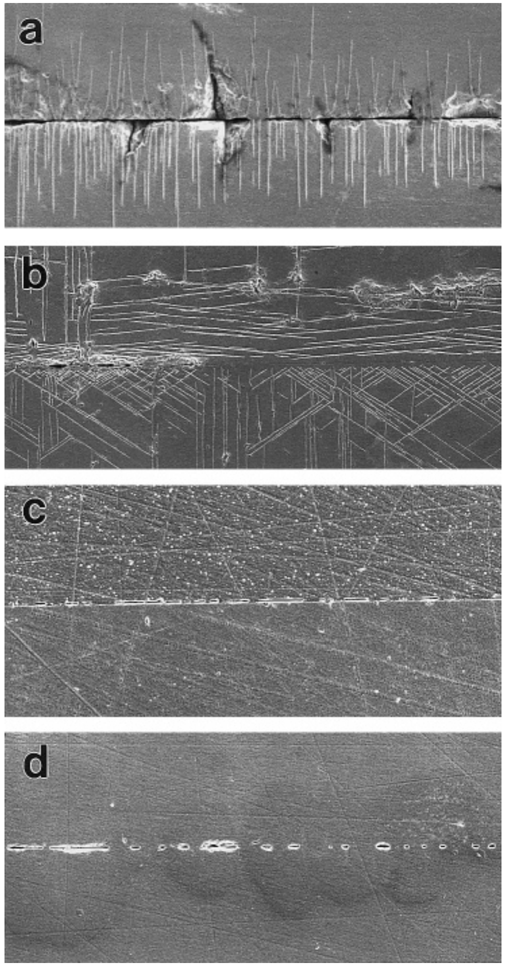



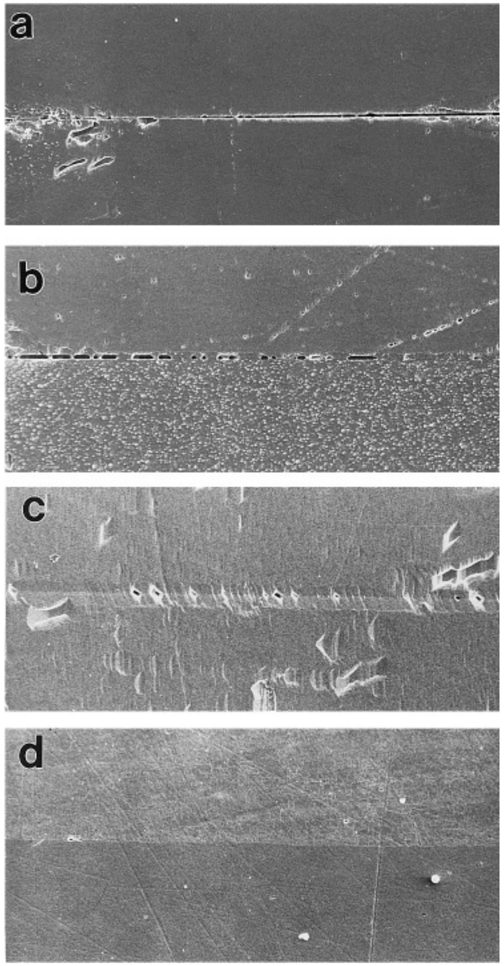

S.C. Byeon, K.S. Hong, Mat.Sci. Eng., A287 (2000) 159-170

# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Electrotransport and sintering – jouining single crystals of ferrite

(a) 900°C, 12 h, no current
(b) 900°C, 12 h, 1 A
(c) 1100°C, 12 h, no current
(d) 1100°C, 12h, 1 A

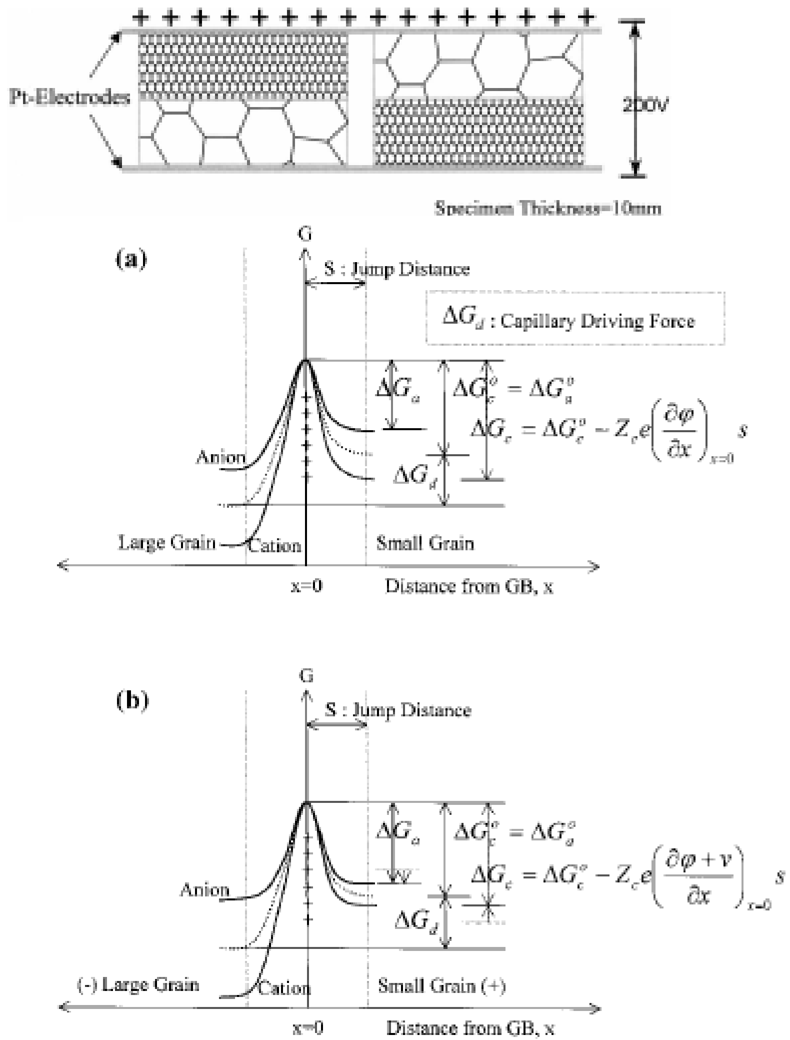


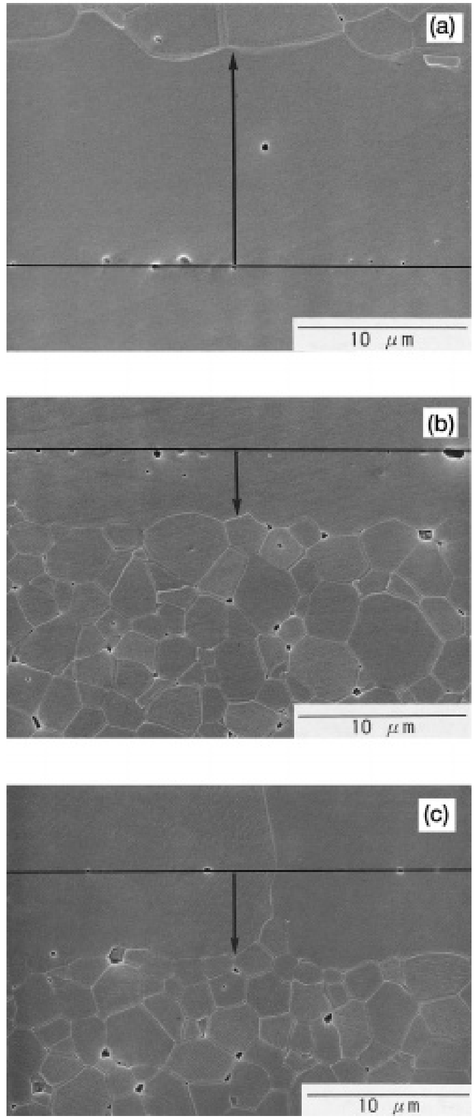




1200°C for:
(a) 3 h, 1 A
(b) 6 h, 1 A
(c) 12 h, 1 A
(d) 24 h, 1 A

S.C. Byeon, K.S. Hong, Mat.Sci. Eng., A287 (2000) 159-170

## Grain boundary migration in alumina



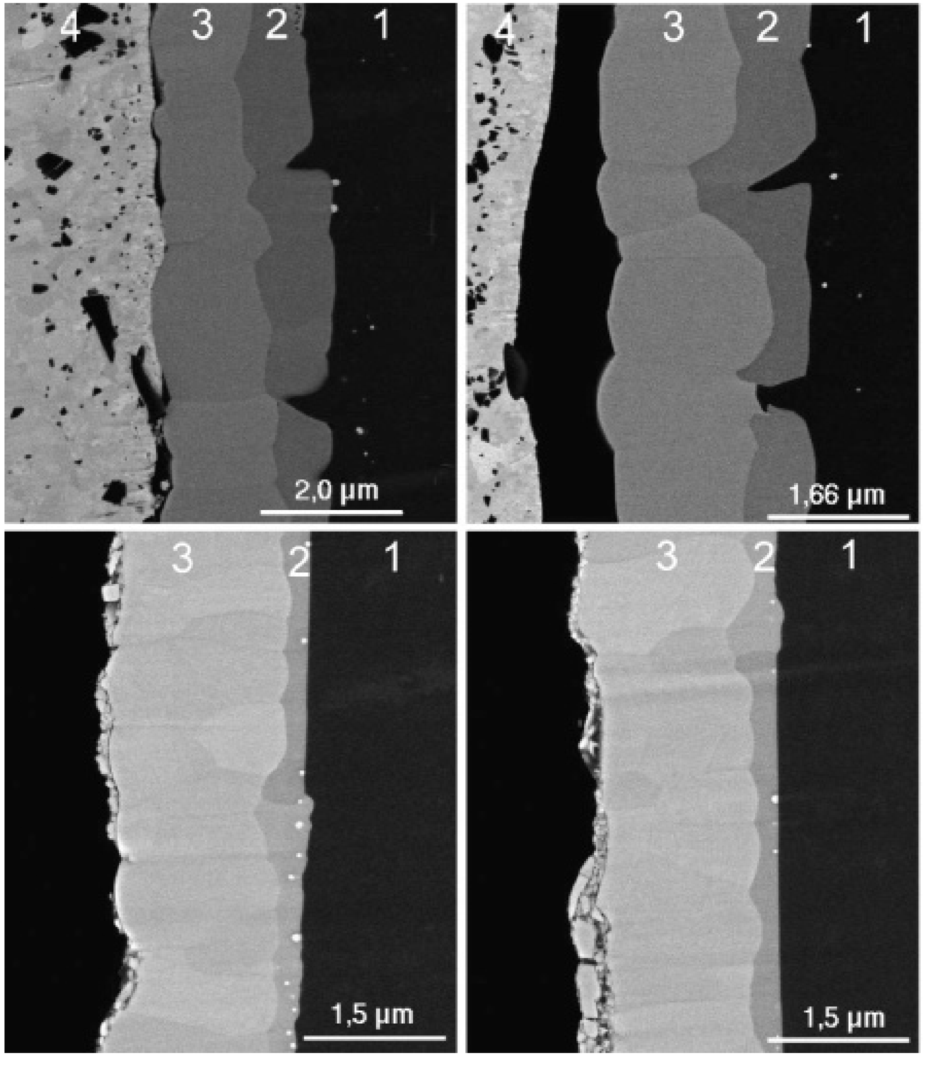




J.-W.Jeong, J.-H.Han, D.-Y.Kim,, J. Am. Ceram. Soc., 83 (2000) 915–18

## FIELD INDUCED DIFFUSION IN IONIC MATERIALS

### Solid state reaction (reactive sintering)

1350°C
12 min
100 V




1350°C
12 min
0 V

(1)MgO
(2) $MgIn_2O_4$
(3) $In_2O_3$
(4) Pt cathode

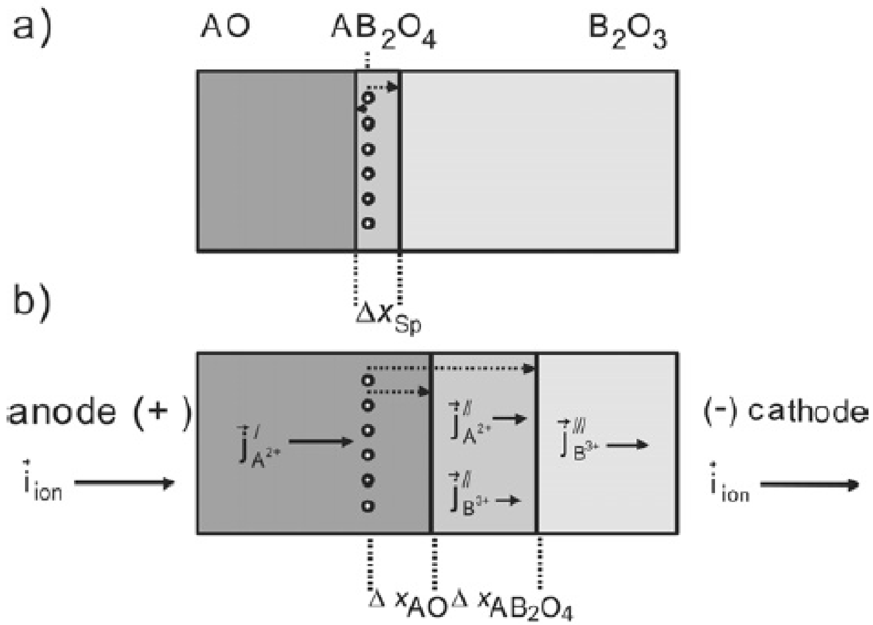
C. Korte, N. Ravishankar, C.B. Carter , H. Schmalzried, Solid State Ionics 148 (2002) 111 –121

# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Solid state reaction (reactive sintering)

$$AO/AB_2O_4: \quad 4AO + 2B^{3+} = AB_2O_4 + 3A^{2+} \quad (1)$$

$$AB_2O_4/B_2O_3: \quad 4B_2O_3 + 3A^{2+} = 3AB_2O_4 + 2B^{3+} \quad (2)$$




- If the ionic current is directed towards $B_2O_3$, the total growth rate is increased. During its growth the spinel layer shifts towards the cathode.
- If the ionic current is directed towards AO, the growth process ends in a steady state with a constant thickness. The steady state derive from the compensation of the electric and the chemical driving forces.

C. Korte, N. D. Zakharov and D. Hesse, Phys. Chem. Chem. Phys., 2003, 5, 5530–5535

# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Cross-correlation between electronic and ionc conduction

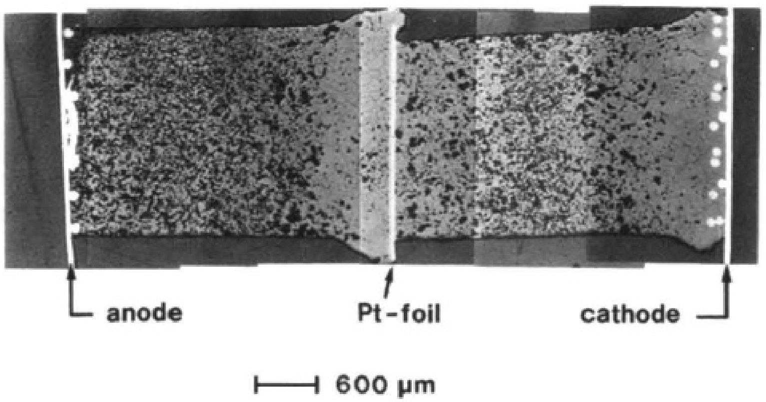
In mixed ionic electronic conductors a flux of mobile ions might be induced not only by a gradient of its own electrochemical potential, but also, indirectly, by a gradient of electrochemical potential of electrons

$$\begin{pmatrix} J_i \\ J_e \end{pmatrix} = -\begin{pmatrix} L_{ii} & L_{ie} \\ L_{ei} & L_{ee} \end{pmatrix} \begin{pmatrix} \nabla \eta_i \\ \nabla \eta_e \end{pmatrix}$$

$L_{ie} = L_{ei}$ Onsager relationship

usually it is considered $L_{ie} = L_{ei} = 0$ meaning that ions and electrons move independently

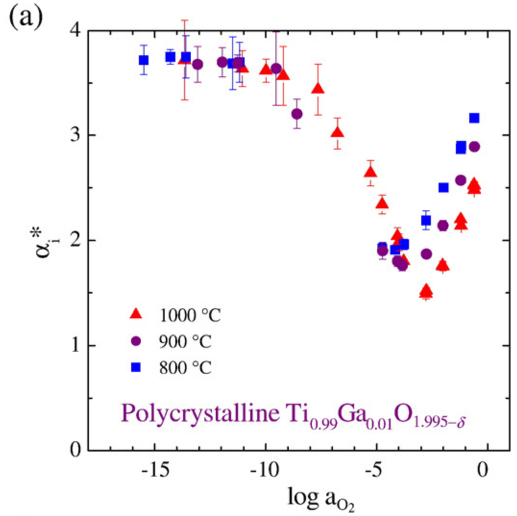
**In some semicondacting oxides this assumption is not valid. This can produce a transfer of matter in presence of intense electronic fluxes**



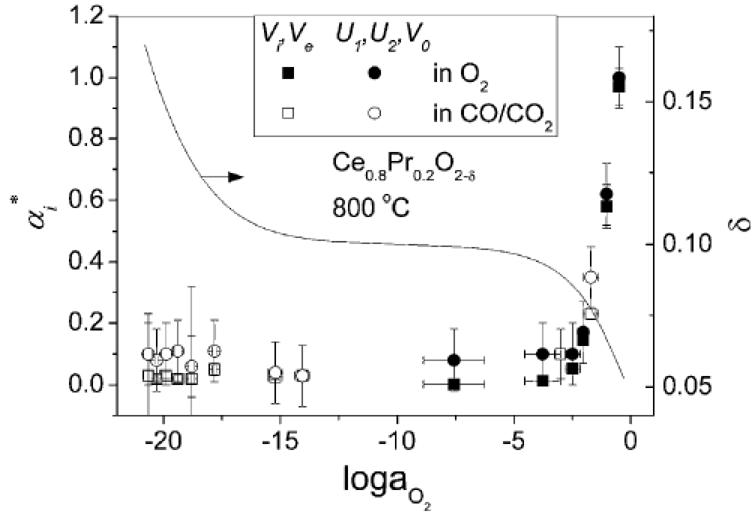

H.-I. Yoo, D.-K. Lee, Solid State Ionics 179 (2008) 837–841

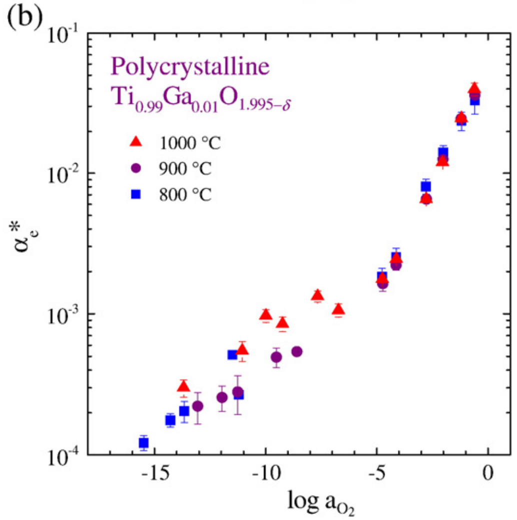
# FIELD INDUCED DIFFUSION IN IONIC MATERIALS

## Cross-correlation between electronic and ionc conduction

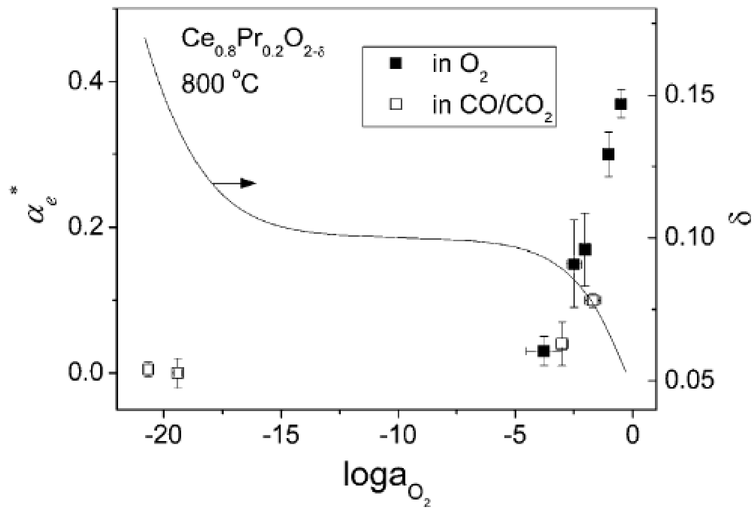



$$\alpha_i^* = \frac{L_{ei}}{L_{ii}} = \left(\frac{J_e}{J_i}\right)_{\nabla \eta_e = 0}$$




$$\alpha_e^* = \frac{L_{ie}}{L_{ee}} = \left(\frac{J_i}{J_e}\right)_{\nabla \eta_i = 0}$$




H.-I. Yoo, D.-K. Lee, Solid State Ionics 179 (2008) 837–841

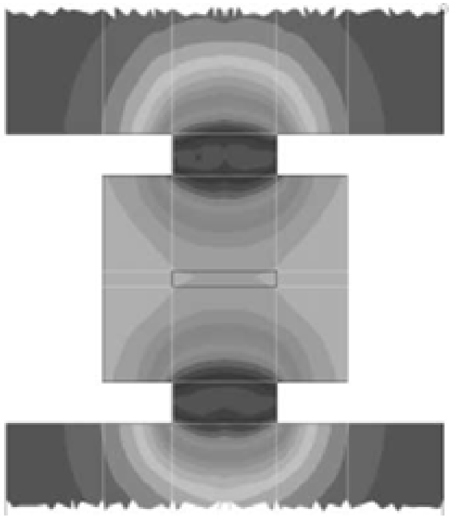
C.Chatzichristodoulou, et al Phys. Chem. Chem. Phys., 2010, 12, 9637–9649

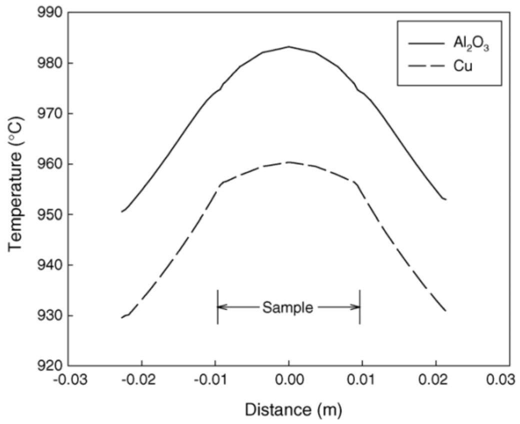
# MECHANISMS IN FAST SINTERING

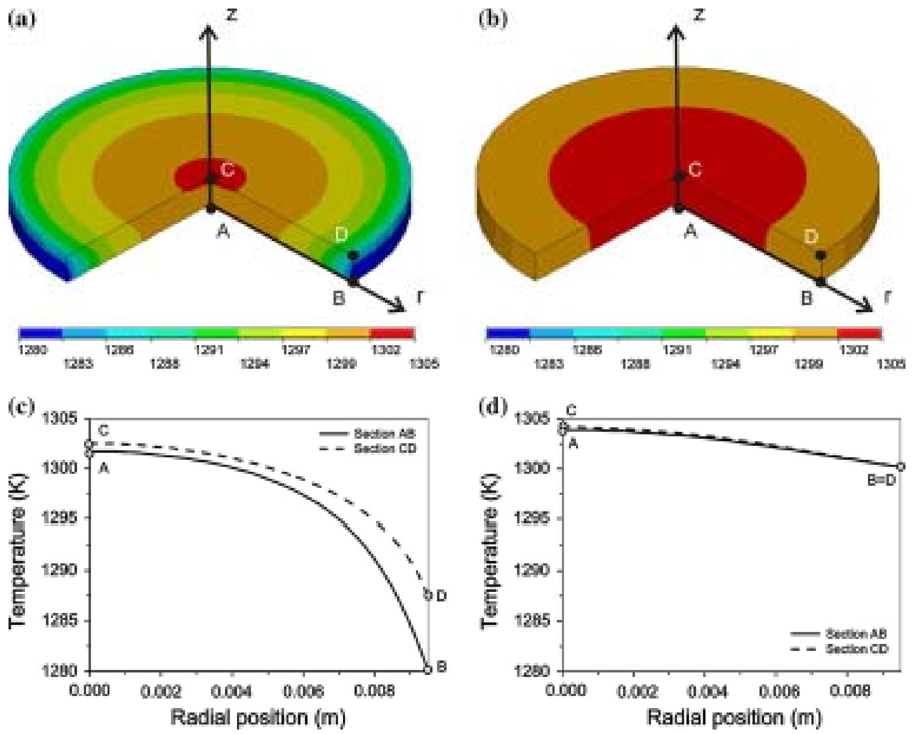
- Arc and spark discharge
- Electromigration
- Electric field induced diffusion
- **Temperature gradients**
- Pressure and stress gradient
- Modification of defects concentration
- Heating rate

# TEMPERATURE GRADIENTS AND DIFFUSION

## Macroscopic temperature gradients






U. Anselmi-Tamburini, S. Gennari, J.E. Garay, Z.A. Munir, Mat.Sci.Eng.A 394 (2005) 139–148

S. Munoz , U. Anselmi-Tamburini, J Mater Sci (2010) 45:6528–6539

# TEMPERATURE GRADIENTS AND DIFFUSION

## Macroscopic temperature gradients

***Soret effect*** (thermotransport or thermomigration)

$$J = -D\frac{\partial C}{\partial x} + uFC$$

$$J = -D\frac{\partial C}{\partial x} - S\frac{\partial T}{\partial x}$$

$$Q^* \equiv \frac{S}{T}$$

Heat of transport

At the steady state

$$\left(\frac{\partial C}{\partial x}\right)_{ss} = -\frac{S}{D}\left(\frac{\partial T}{\partial x}\right)_{ss}$$

*S* can be either negative or positive

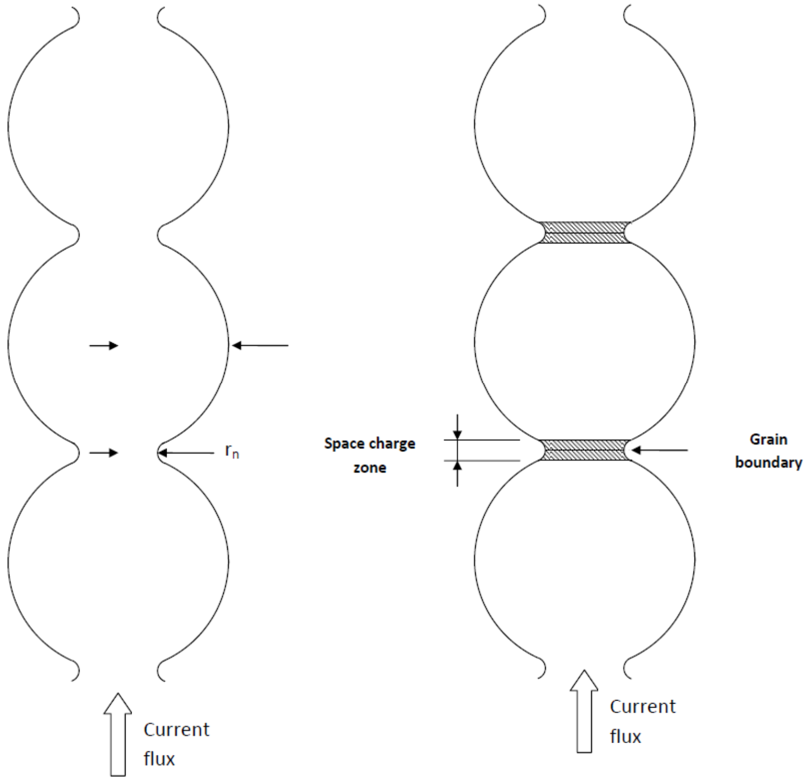
For vacancy distribution in a metal $h_{fv}$ enthalphy of formation for a vacancy

$$J_v = -\frac{D_v N c_v \nabla T}{kT^2}\left(h_{fv} + q_v^*\right)$$

## Microscopic temperature gradients

Within the single grain. Two main causes:

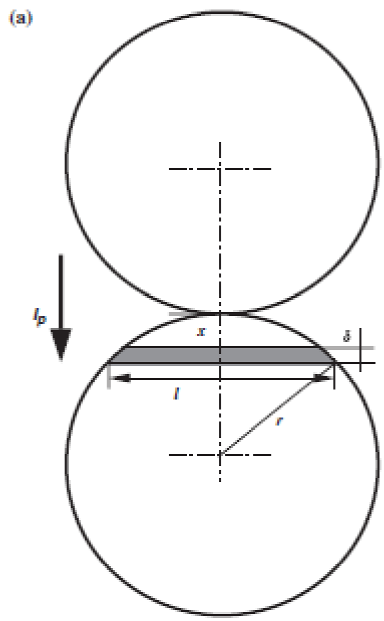
1) Cross section restriction
2) Grain boundary resistance

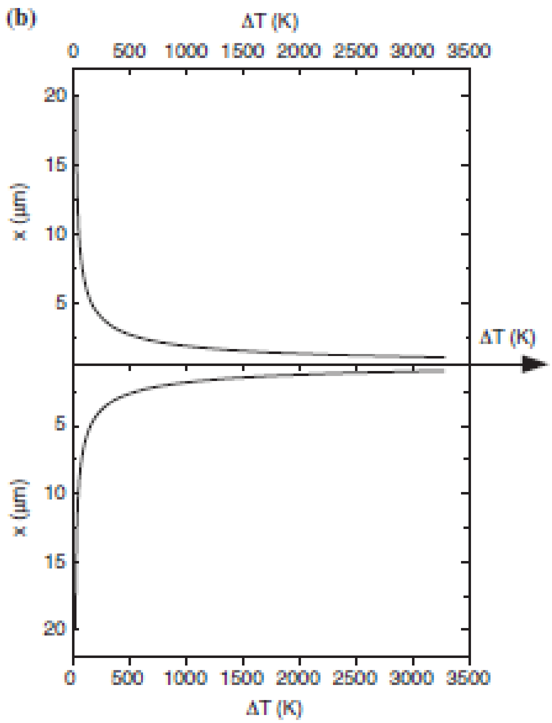


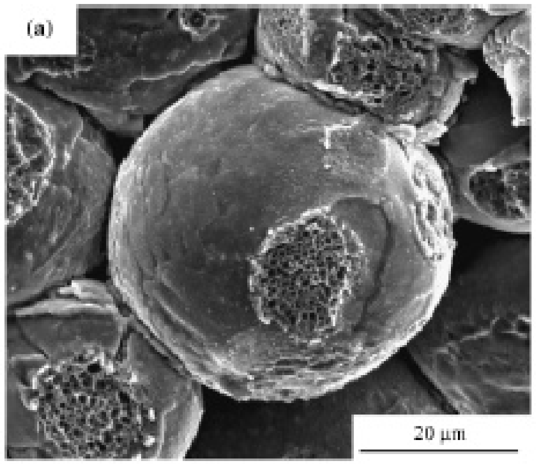

It has been suggested that microscopic temperature gradients are related to flash sintering and to retarded grain growth

# TEMPERATURE GRADIENTS AND DIFFUSION

## Microscopic temperature gradients – cross section restriction




Localized Soret effect

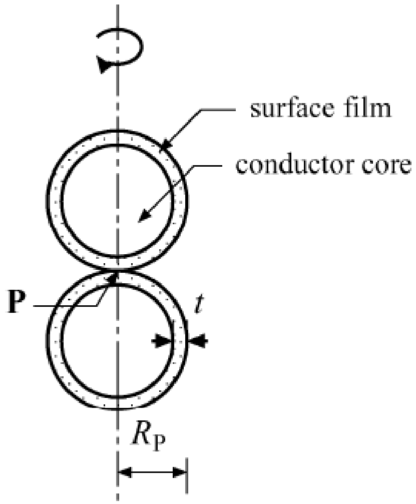
Localized enhanced diffusivity, melting and vaporization

X.Song, X. Liu, J.Zhang, J. Am. Ceram. Soc., 89 [2] (2006) 494–500

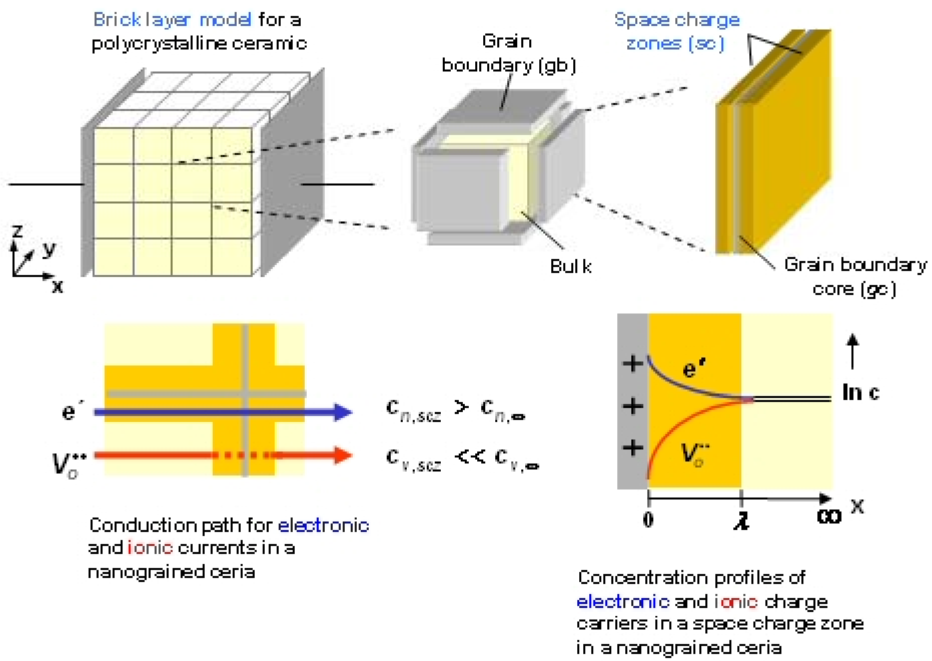
# TEMPERATURE GRADIENTS AND DIFFUSION

## Microscopic temperature gradients – grain boundary resistance

metals




Ionic materials




S. Kim and J. Maier, *J. Electrochem. Soc.*, 149 (10), J73 (2002).

# MECHANISMS IN FAST SINTERING

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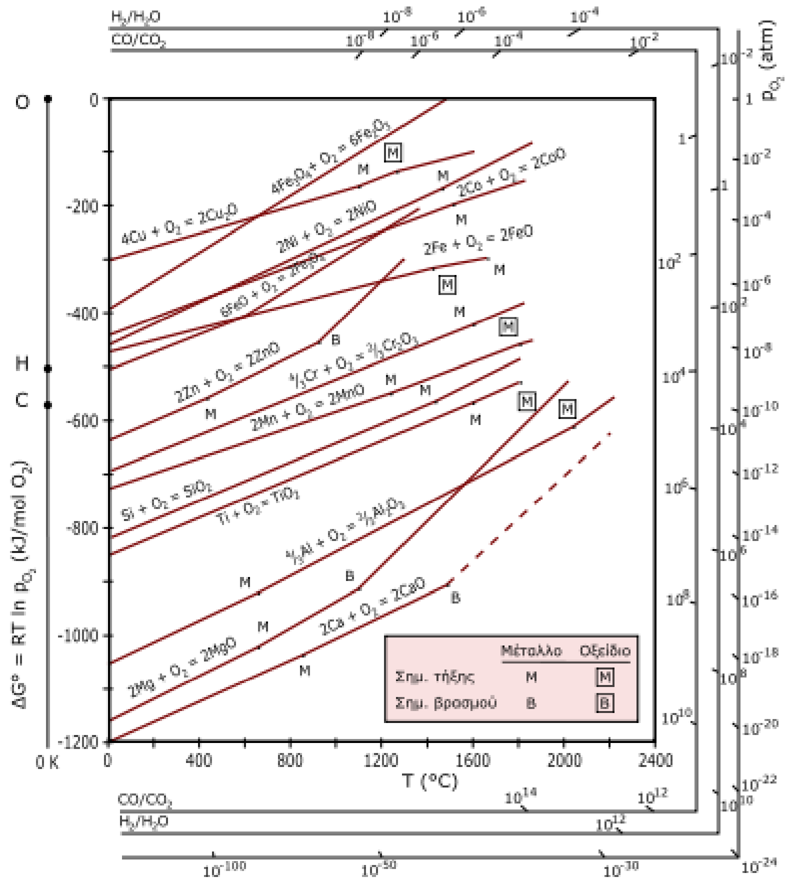
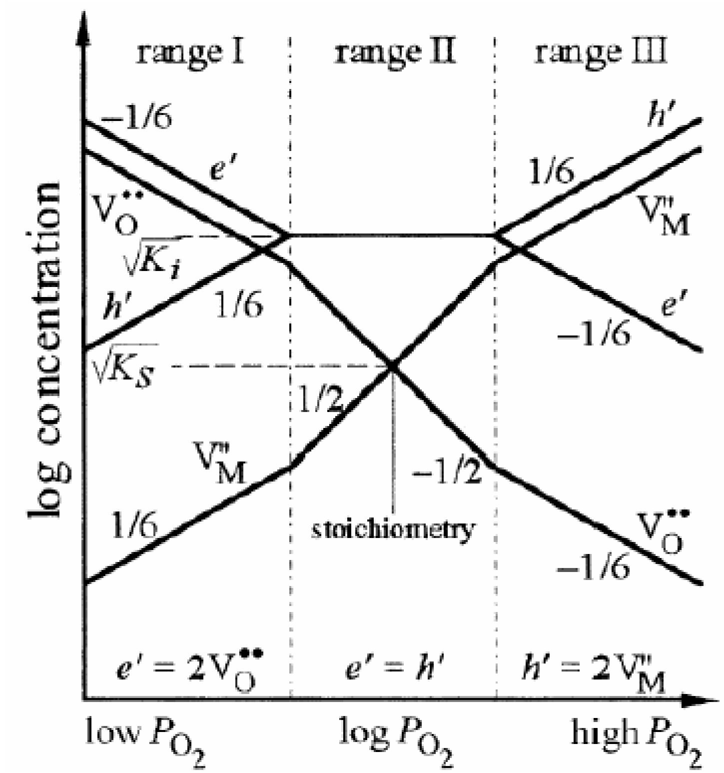
- Heating rate

# MODIFICATION IN DEFECTS CONCENTRATION

FAST envornment is strongly reducent

It can produce oxygen substoichimetry or even complete reduction



# BASIC MECHANISMS INVOLVED IN FAST SINTERING

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