Some fundamentals on Spark Plasma Sintering as a processing tool to fabricate Biomaterials

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Overall Structure of slide presentation

- ✓ Fundamentals
- ✓ Fundamentals of Sintering as a process to consolidate powders
- ✓ Spark Plasma Sintering : Process description
- ✓ Spark Plasma Sintering : Simulation results

Broad objectives:

The series of slides serve following objectives:

- **The fundamental concepts of Sintering Process**
- **Process description of Spark Plasma Sintering**
- **Spark Plasma Sintering Process Simulation results**

Some background on Nanoceramics and Nanocomposites

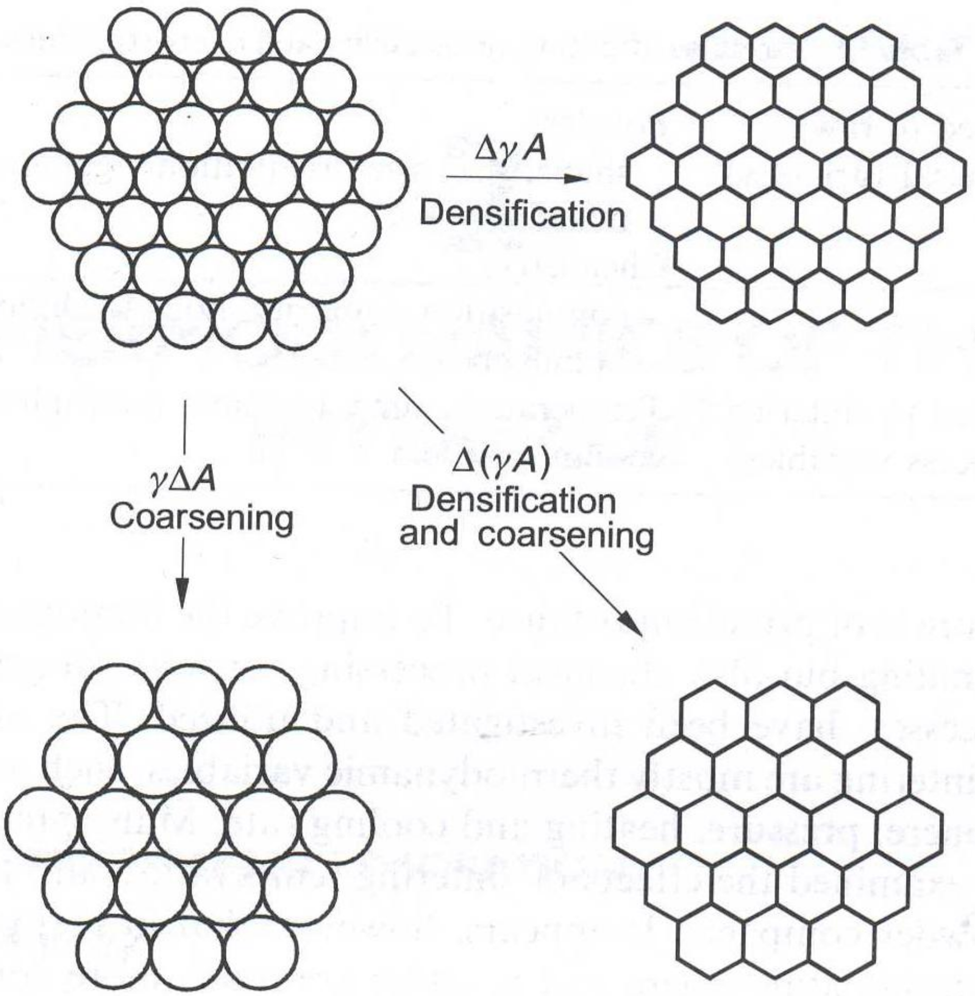
Sintering

Sintering refers to the process of firing and consolidation of powders at T> $0.5T_m$, where diffusional mass transport leads to the formation of a dense body.

Classification:

- **Solid state sintering**
- **Liquid phase sintering**

Basic phenomena occurring during sintering under the driving force for sintering



Global Thermodynamic Driving Force

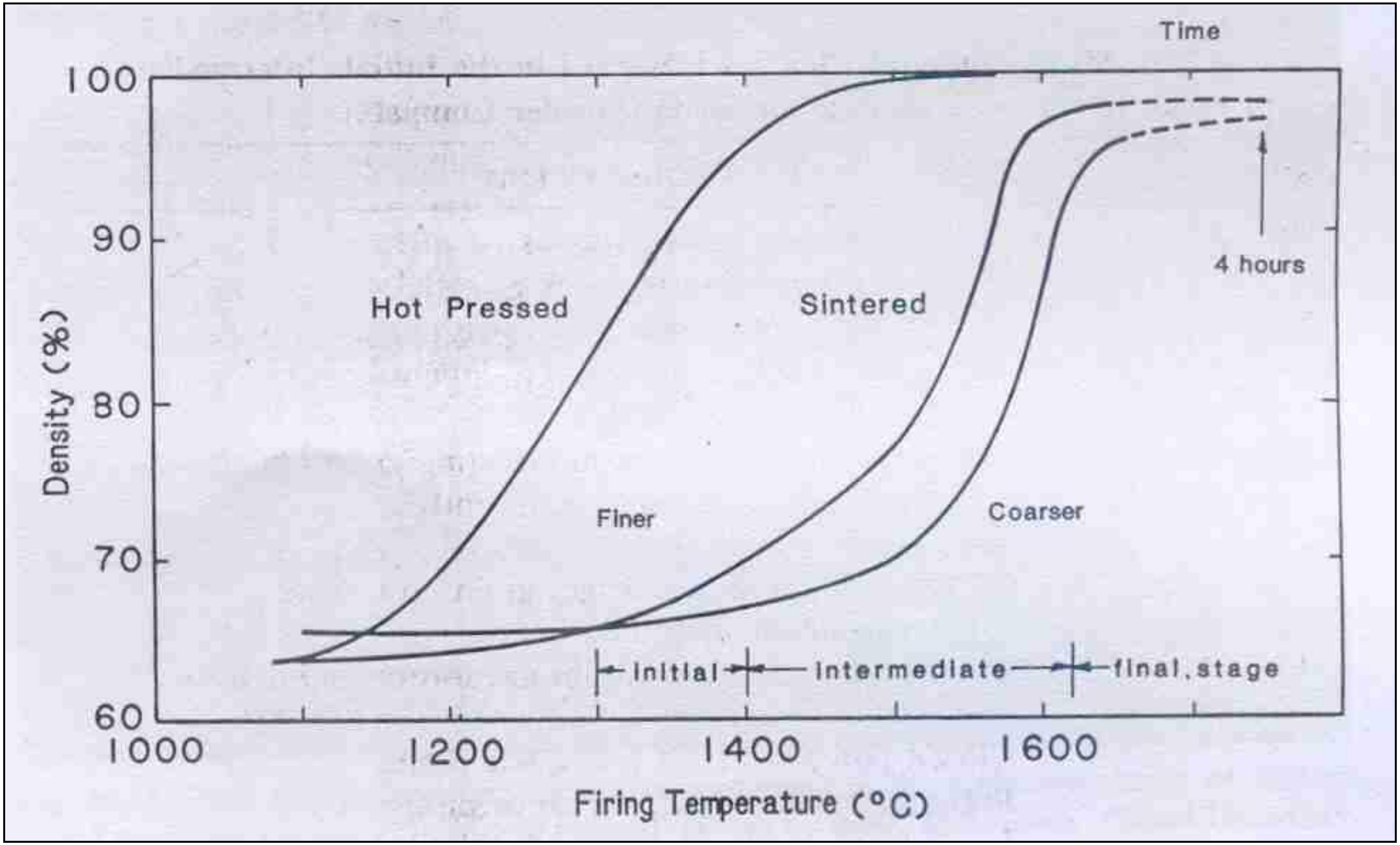
- Sintering is an irreversible process in which total free energy of the system is decreased by decreasing total surface area i.e. replacing S/V interfaces with S/S interfacial area.

$$dG = \gamma_{ss} dA_{ss} + \gamma_{sv} dA_{sv} < 0$$

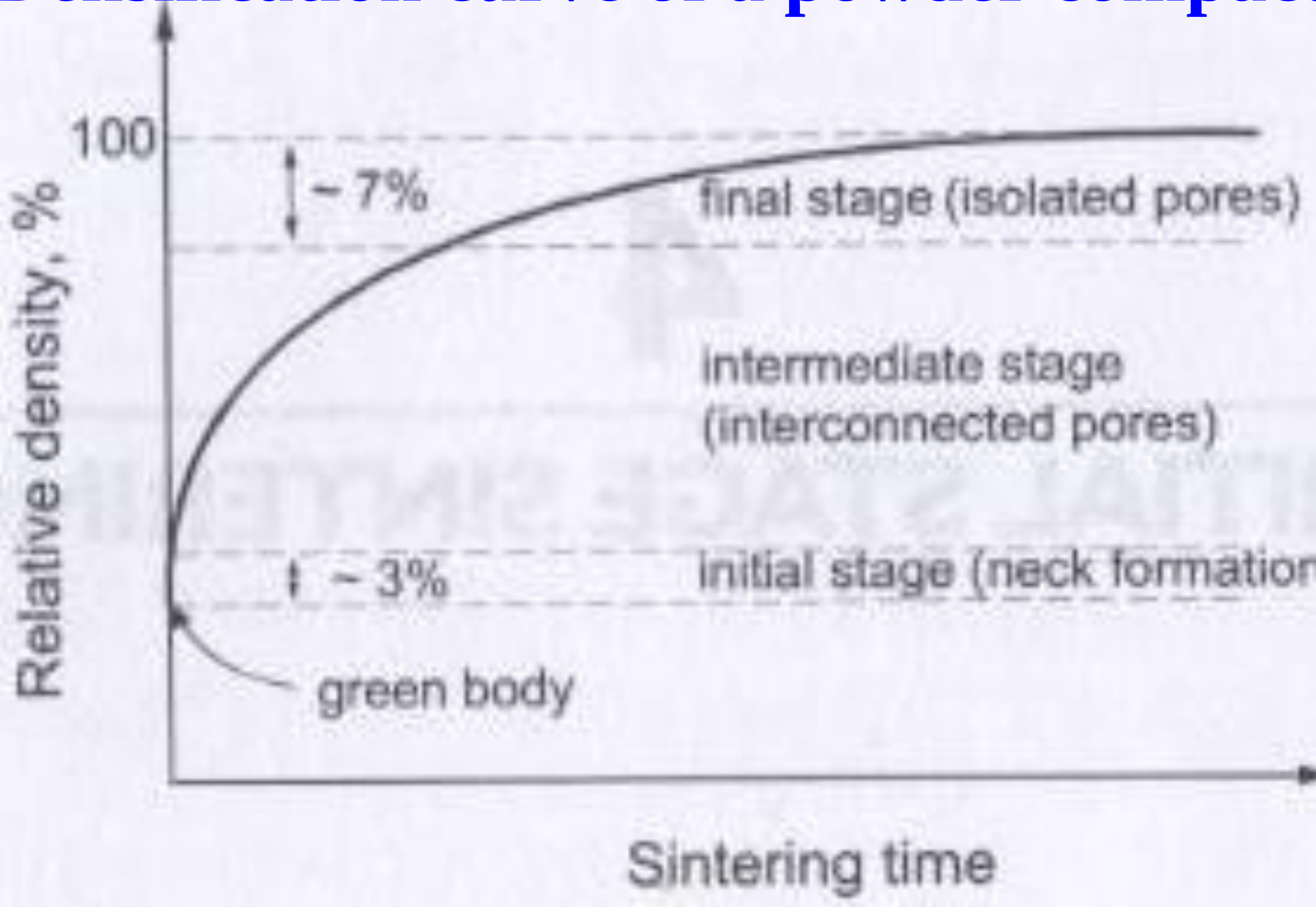
Sintering will stop, when dG = 0

$$\Rightarrow \frac{\gamma_{ss}}{\gamma_{sv}} = -\frac{dA_{sv}}{dA_{ss}}$$

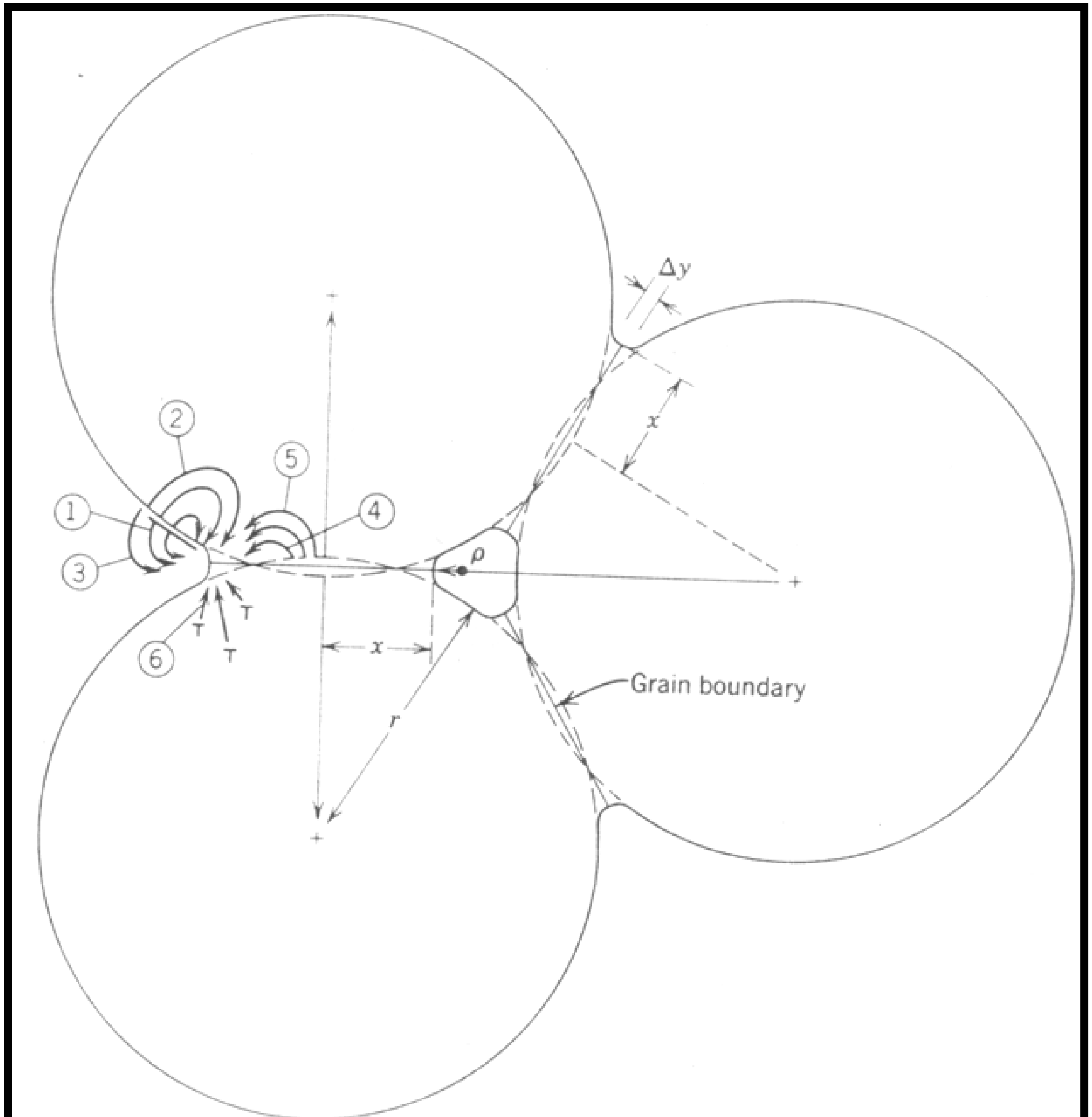
Densification during sintering



Densification curve of a powder compact



Sintering Mechanisms: Three particle model



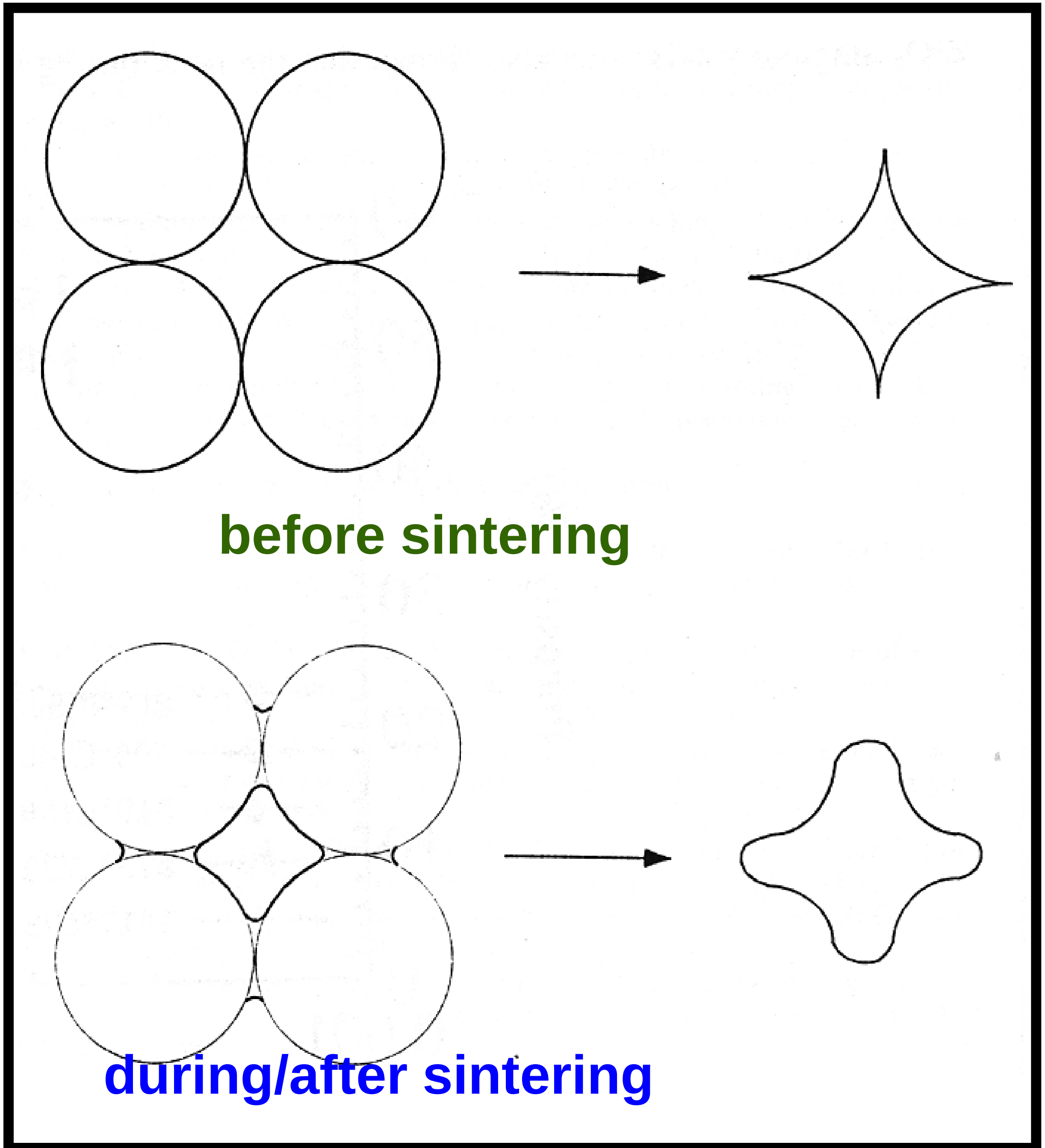
- ❑ Rate limiting stage in solid state sintering is the diffusion of slowest diffusing ions along its fastest path

- ❑ Ambipolar diffusion occurs in case of ionic solids

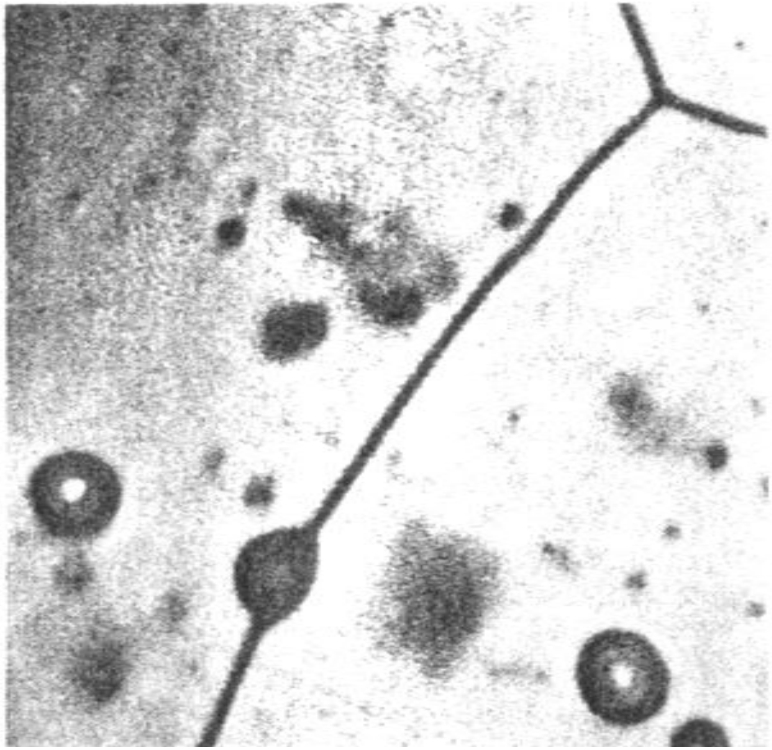
- ❑ Surface diffusion leads to particle coarsening, instead of shrinkage

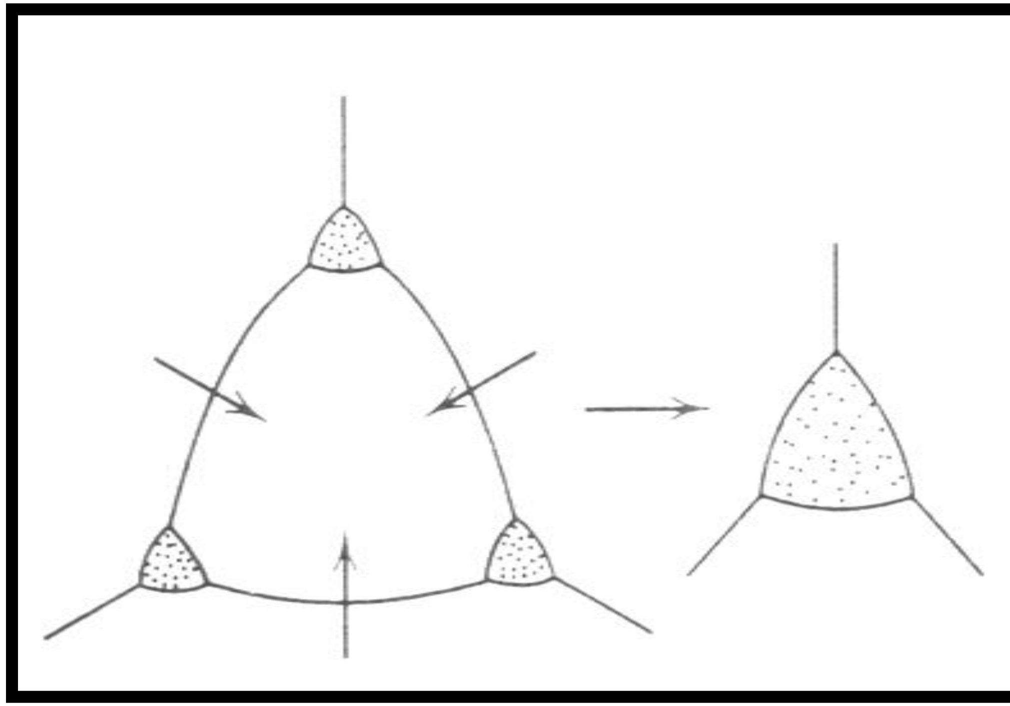
- ❑ Only lattice diffusion (at final stage) and GB diffusion (mostly in intermediate stage) leads to densification.

Pore size/shape during sintering



Pore movement and pore shape during grain growth

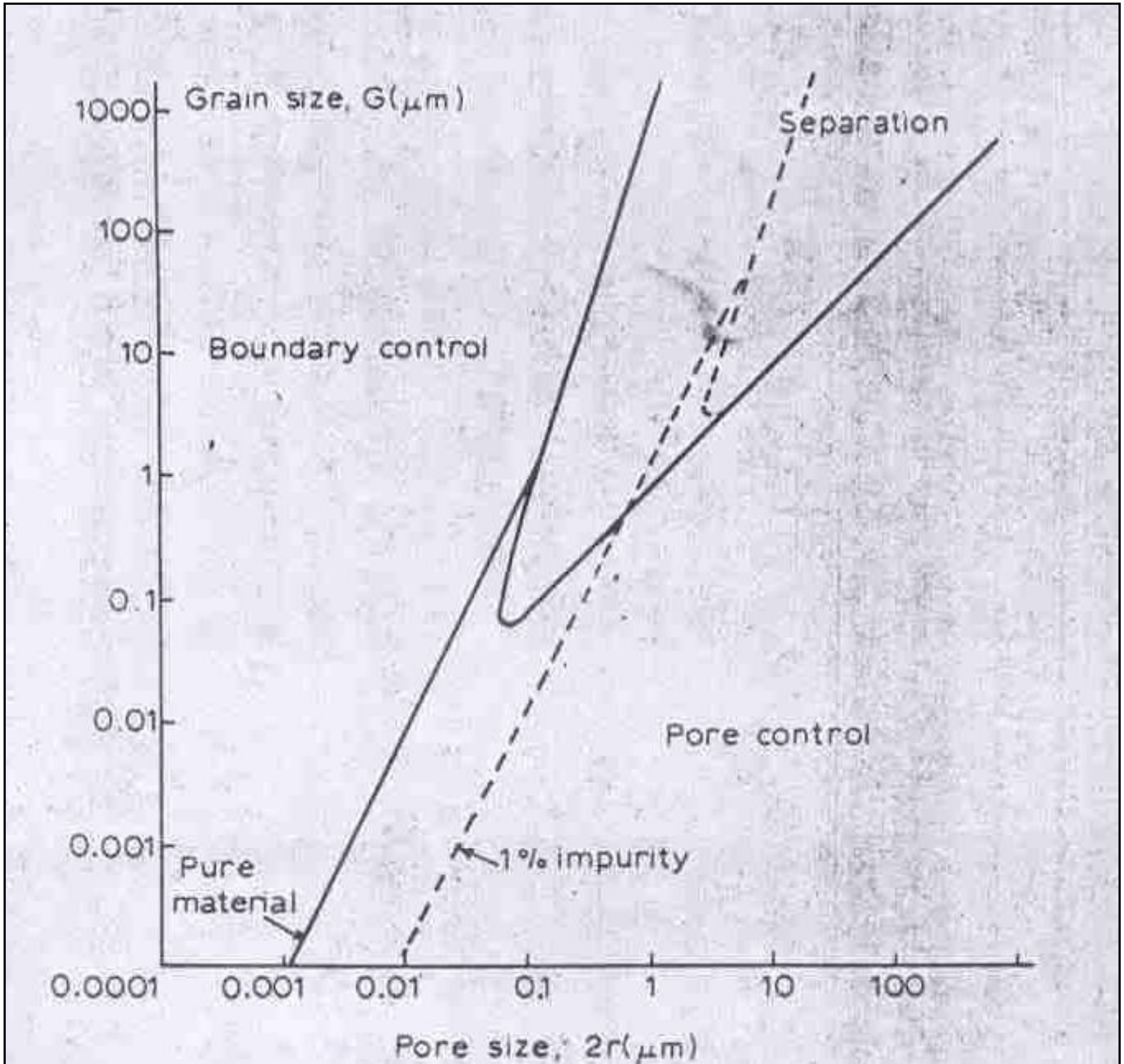




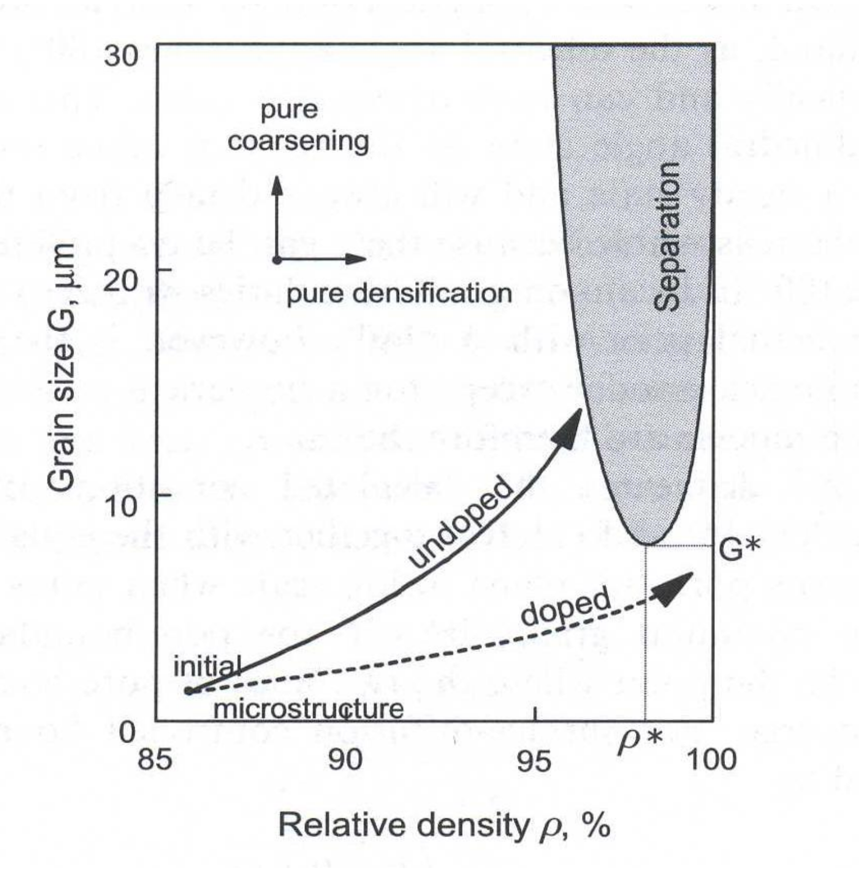
❑ Pore morphology changes during grain boundary migration for pores attached to grain boundary. The total elimination of porosity depends on the location of pores, pore size as well as on densification-grain size trajectory

❑ The grains at triple junctions shrink and resultantly, pores coalesce leading to decrease in number of pores and pore growth

Pore-separation during sintering

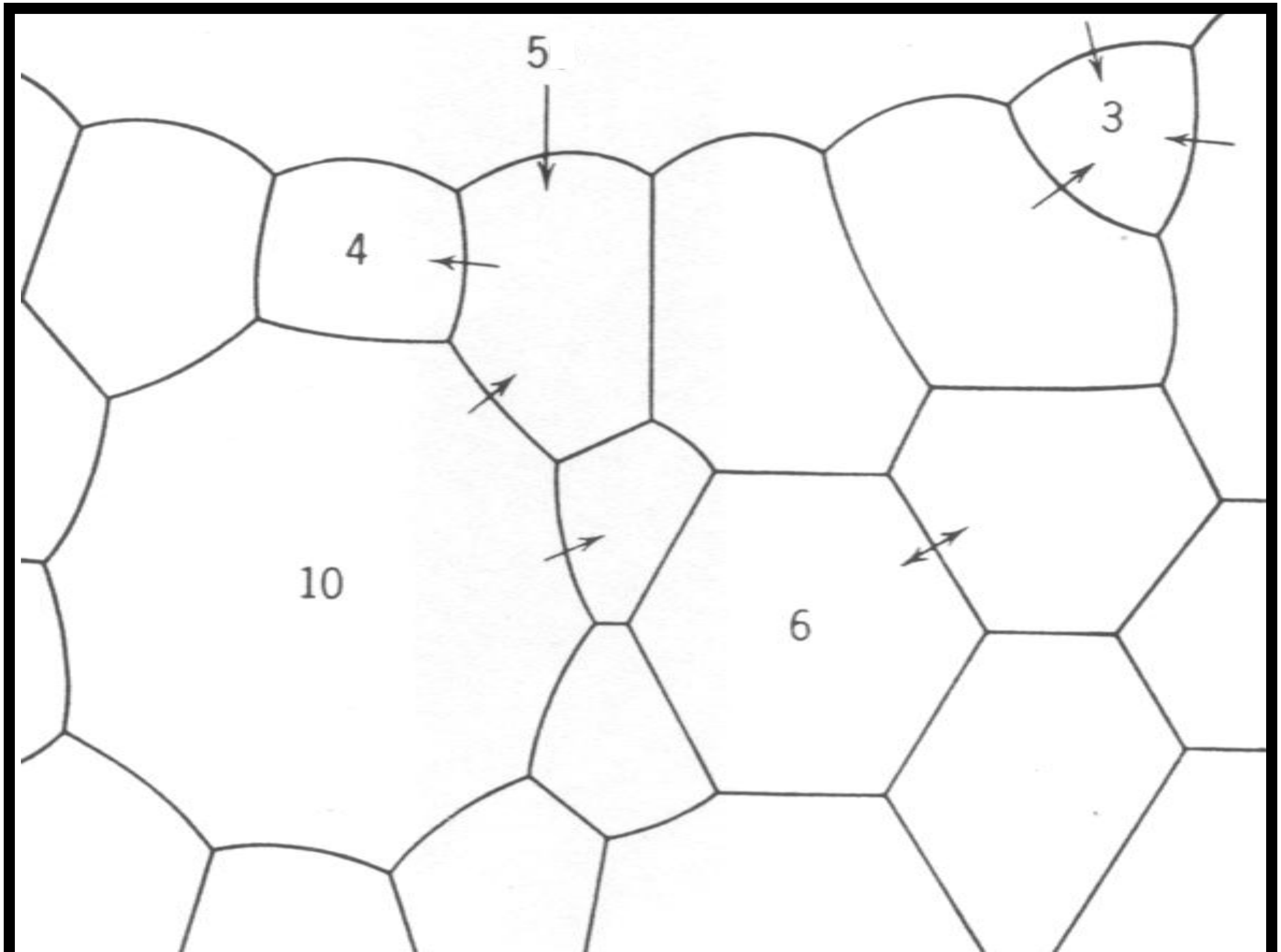


Schematic of microstructure development in terms of a plot of grain size versus density



Grain growth in ceramics

Normal/Continuous Vs. Abnormal/discontinuous/exaggerated grain growth



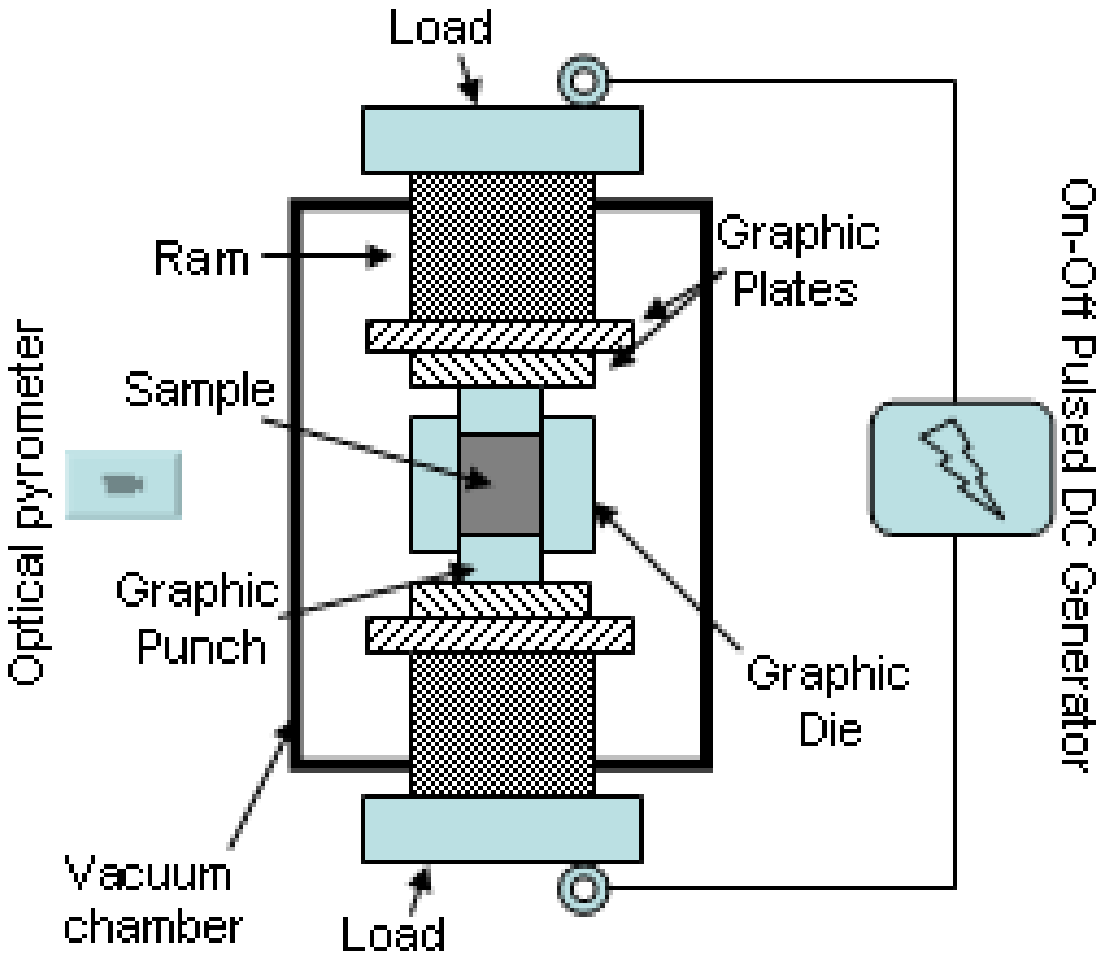
- ❑ The grains with 6 grain edges: Equiaxed grains without any curvature
- ❑ The grains with < 6 sides or grain edges shrink due to

SPS process has major relevance to fabrication of Nanoceramics and Nanoceramic composites

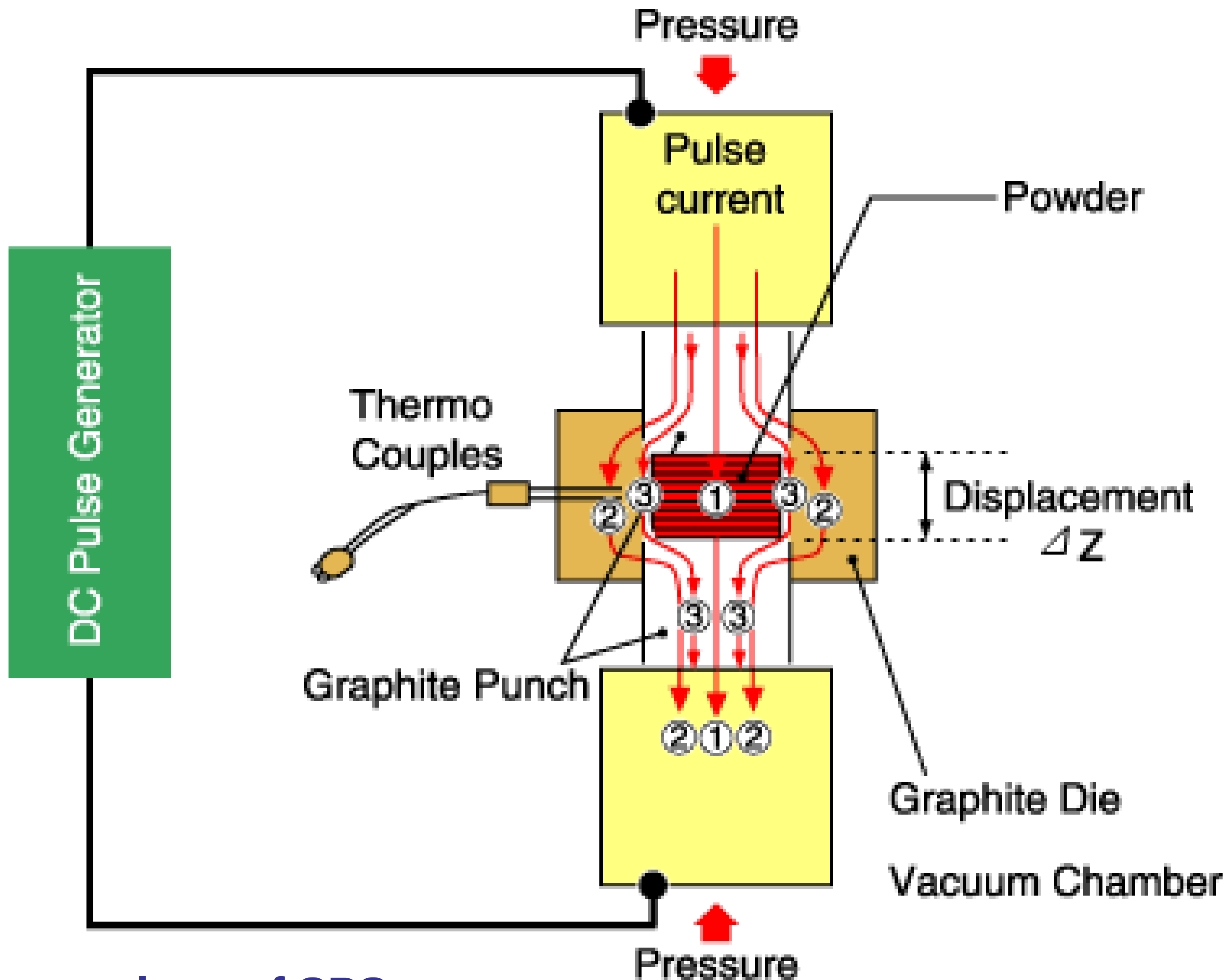
Spark plasma sintering (SPS)

Benefits:

- ❖ Reduced sintering time.
- ❖ Good grain to grain bonding.
- ❖ Clean grain boundaries.



- ❖ Initial activation of powders by pulsed voltage.
- ❖ Resistance sintering under pressure.



Phenomenology of SPS:

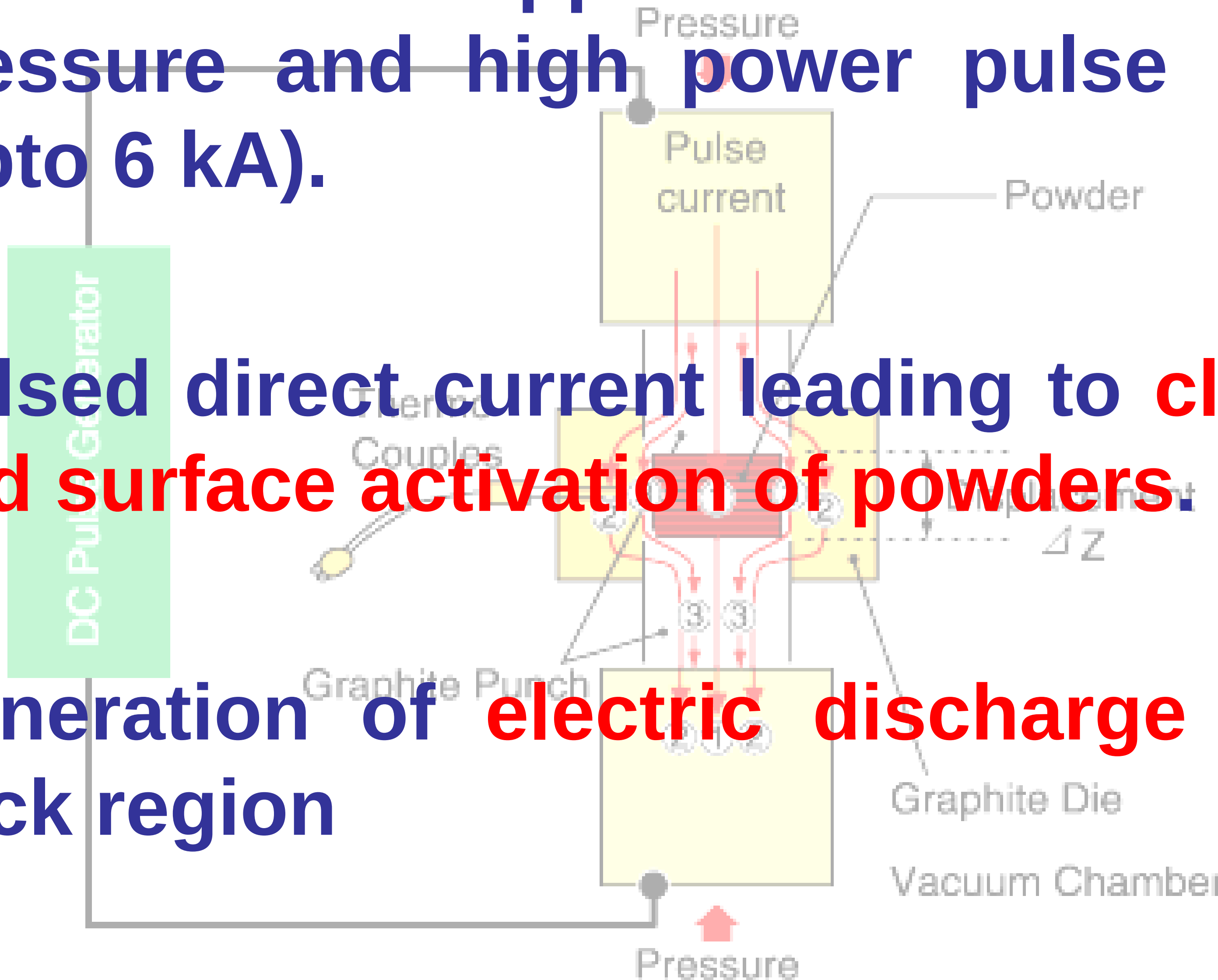
- release of electrical energy through a porous powder compact
- breakdown of surface films
- Arcing at pores leading to enhanced mass transport to neck

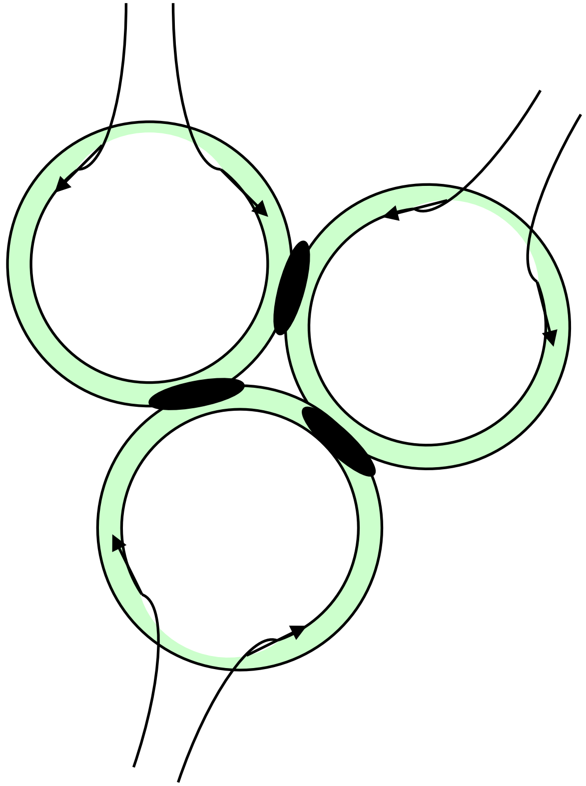
SPS effect

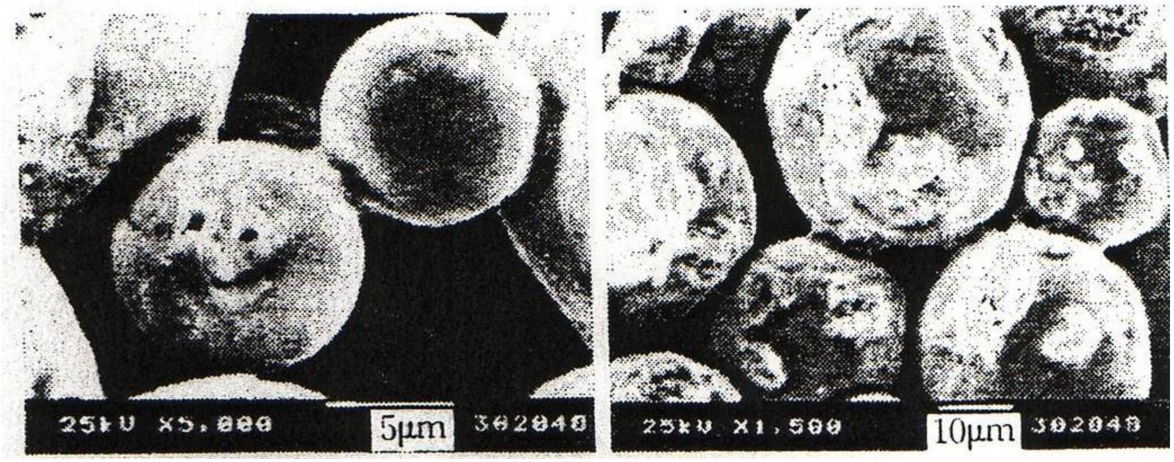
- Simultaneous application of mechanical pressure and high power pulse source (upto 6 kA).

- Pulsed direct current leading to **cleaning and surface activation of powders.**

- Generation of **electric discharge** at the neck region







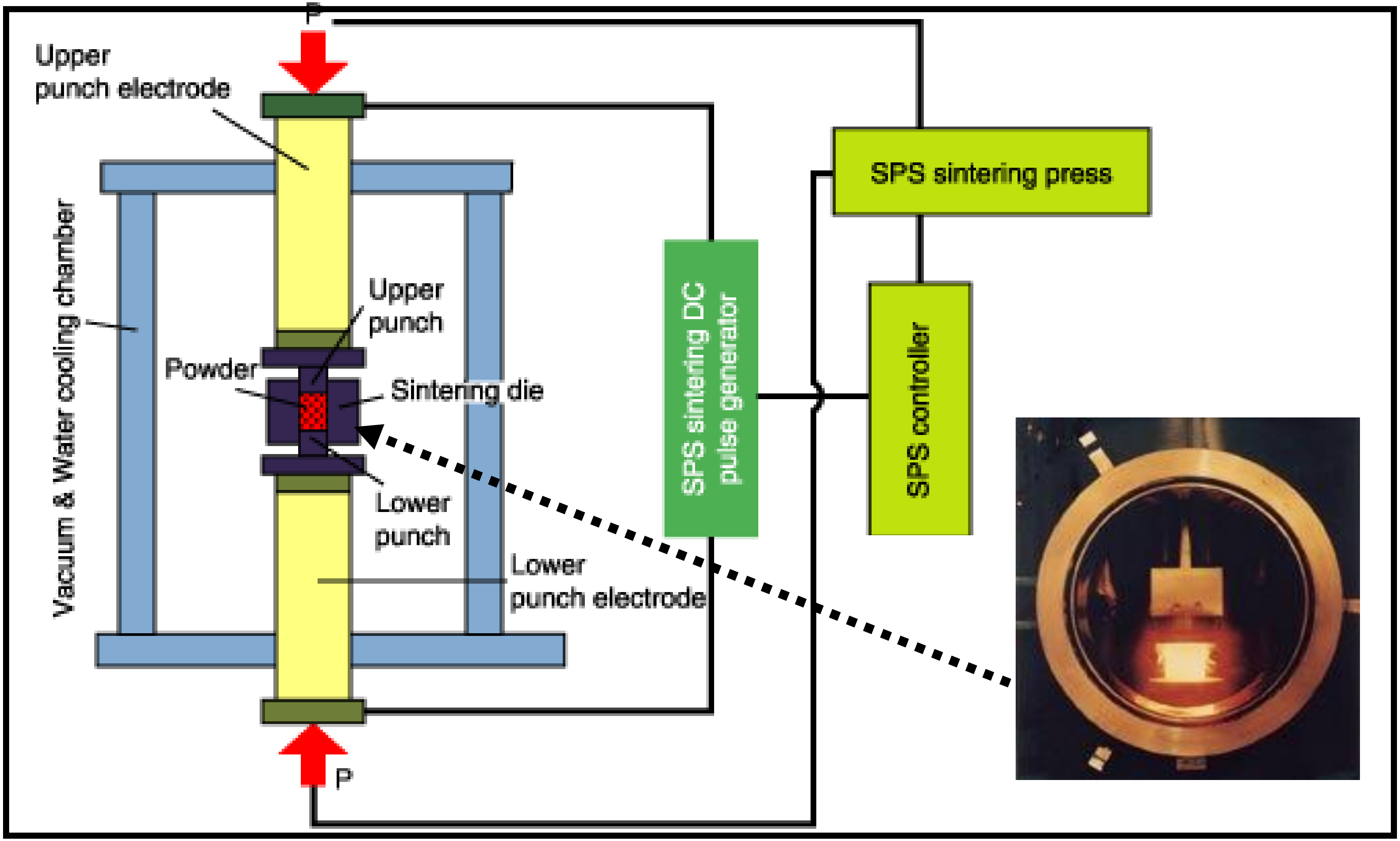
Neck formation due to localized heating

Joule's heating: localized temperature increment

Groza et al., UC Davis

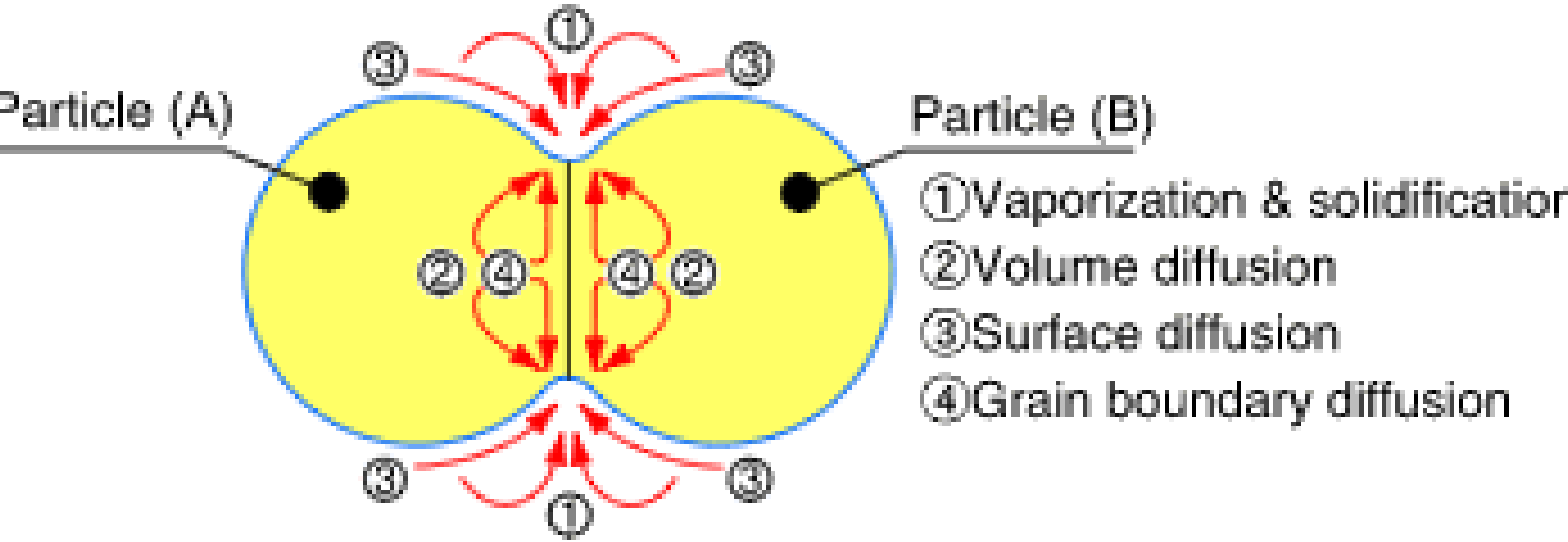
In the presence of pressure and electric current, localized necking occurs faster due to joule heating. Consequently, the temperature raises very fast (faster than conventional sintering and Hot pressing) and the densification is completed within few minutes

Experimental: Spark Plasma Sintering

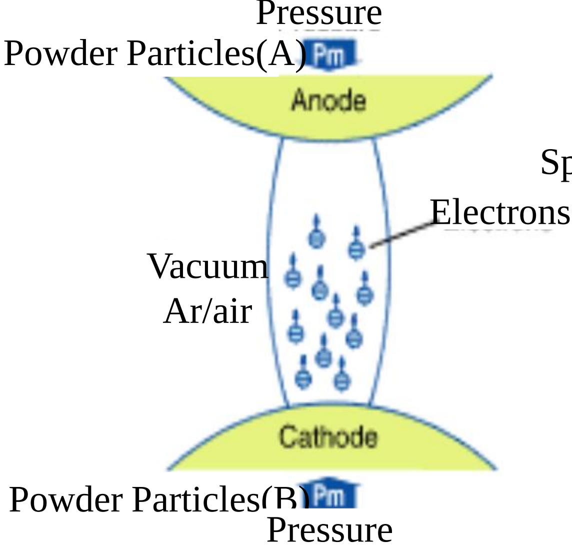


Heating rate : 600 – 650 K/min;
DC Voltage : 5 – 10 V;
Vacuum: 60-70 mtorr;

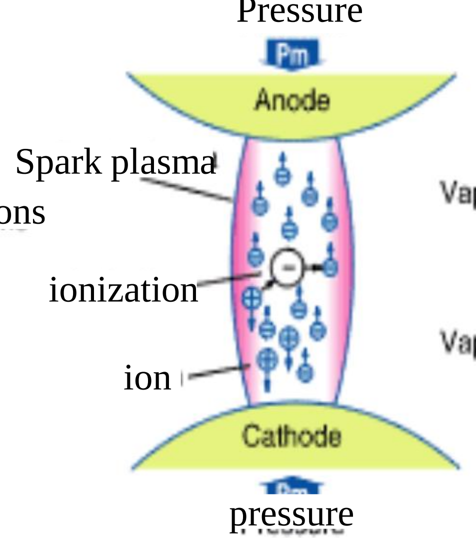
Maximum pressure: 50-60 MPa
Pulse frequency: 30-40 kHZ
Sintering time: 5 minutes



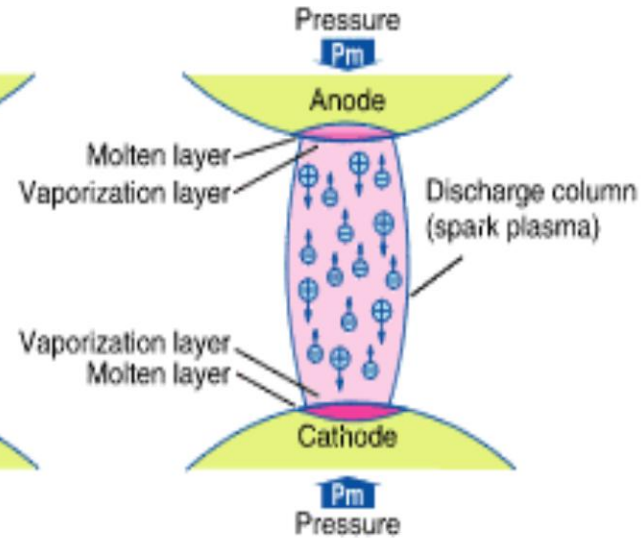
When spark discharge appears in the gap between the particles of a material, a local high temperature state occurs. This causes vaporization and the melting of the surfaces of the powder particles during the SPS process; constricted shapes or "necks" are formed around the contact area between the particles. These necks gradually develop and plastic transformation progresses during sintering, resulting in a sintered compact of over 99% density. Since only the surface temperature of the particles rises rapidly by self-heating, particle growth of the starting powder materials is controlled.



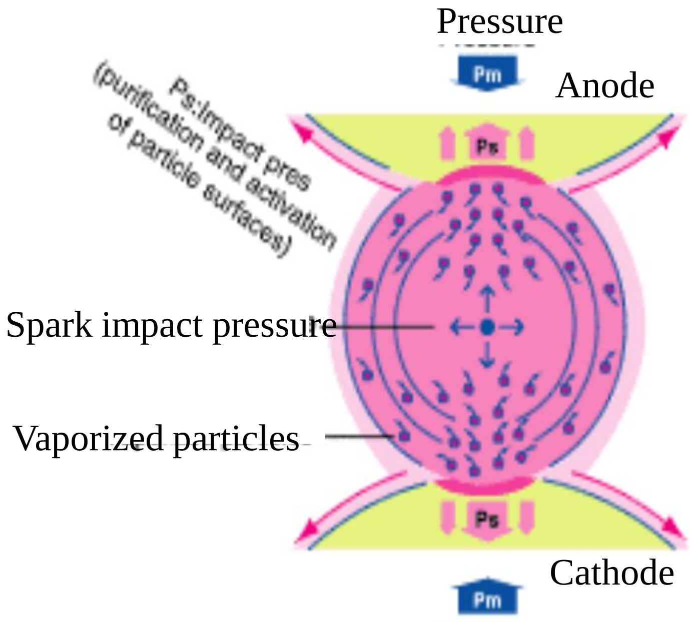
(I) Initial stage of spark discharging by ON-OFF pulse energization

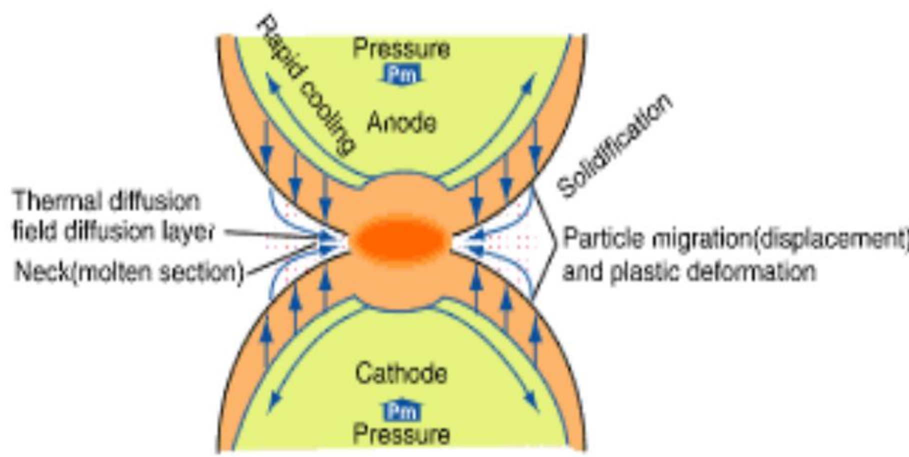


(II) Generation of spark plasma



(III) Vaporization and melting action on the particles surface





(IV) Generation of spark impact pressure, sputtering of vaporized/molten particles

(V) Enhanced neck growth in the presence of spark plasma

SPS process (contd..)

- **The pulsed discharge achieved by the application of an on/off low voltage (~ 30 V) and high current (> 600 A). The duration of each pulse varies between 1 and 300 ms, between 2 and 30 ms.**

- **The subsequent step comprises the application of a DC current at a level dependent on the powder type. The pulsed and direct current may be applied simultaneously or sequentially.**

- **For SPS Process, electrical discharge per se does not consolidate powders and, therefore, some additional effects are needed to increase the final density (pressure application and/or higher temperature than that created by electrical discharge**

- **Pressure applied at constant/variable level during the process.**

- **SPS sintering temperatures range from <u>low to over 2000ºC,</u> which are typically ~ 200-500ºC lower than conventional sintering**

- **Vaporization, melting and sintering completed in short periods of ~ <u>5-20 minutes</u>, including temperature rise and holding times**

Physics of SPS process

- Formation of small capacitors at the contact between particles/at gap around the contact.

- Electrical discharges are generated across these capacitor gaps. The interfering surface oxide films are pierced beyond a certain voltage level, depending on the dielectric strength of oxide layer. This takes place when the arcing across the particles leads to achieving the breakdown voltage and electrical breakdown of dielectric film on the powder particle surface.

- Alternatively, the electrical discharges around the contacts may generate plasma, that is, an ionized gas between the powder particles.

- The above phenomena collectively contribute to the physical activation of the powder particle surface. The physical activation combined with faster densification at lower temperatures reduces grain coarsening and retains a finer microstructure.

SPS process

- **Three mechanisms may contribute to field assisted sintering:**

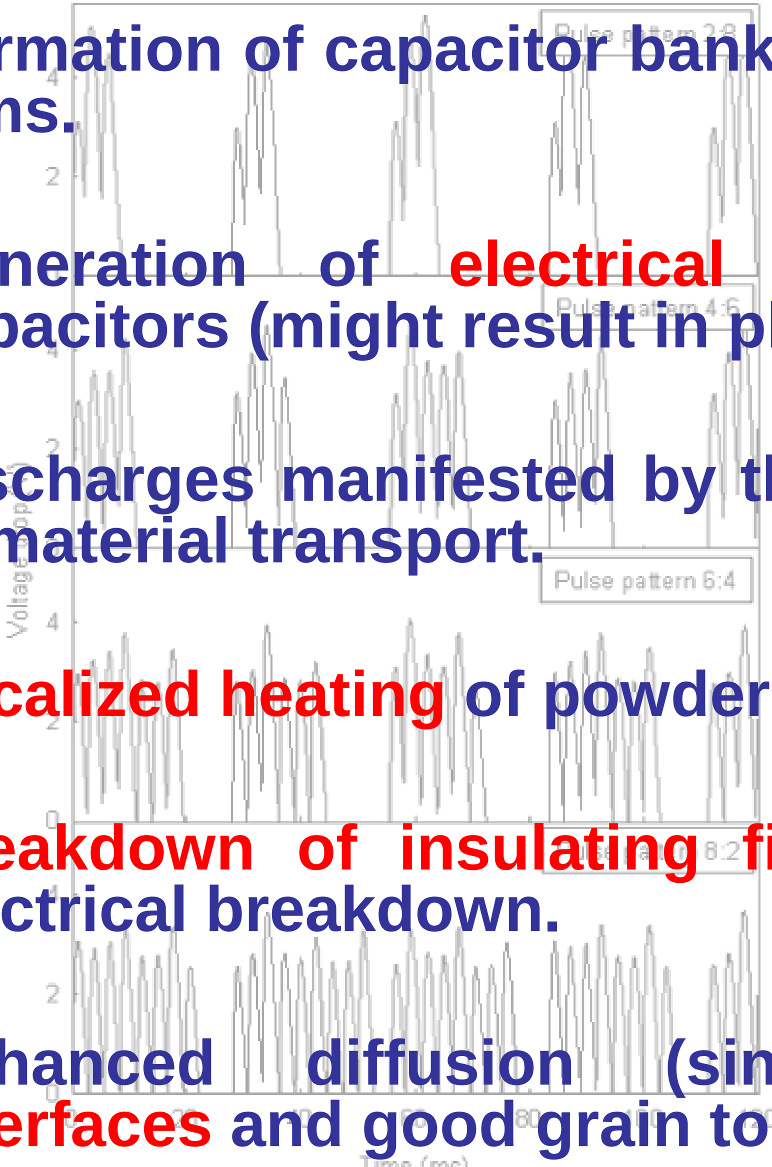
  - activation of powder particles by pulsed current
  - resistance sintering
  - pressure application

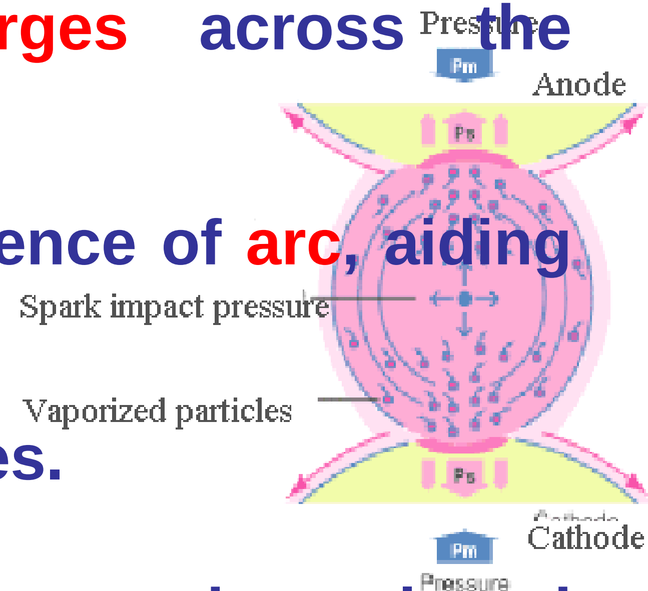
- **This activation is unique and provides main difference from more conventional resistance sintering processes (hot pressing).**

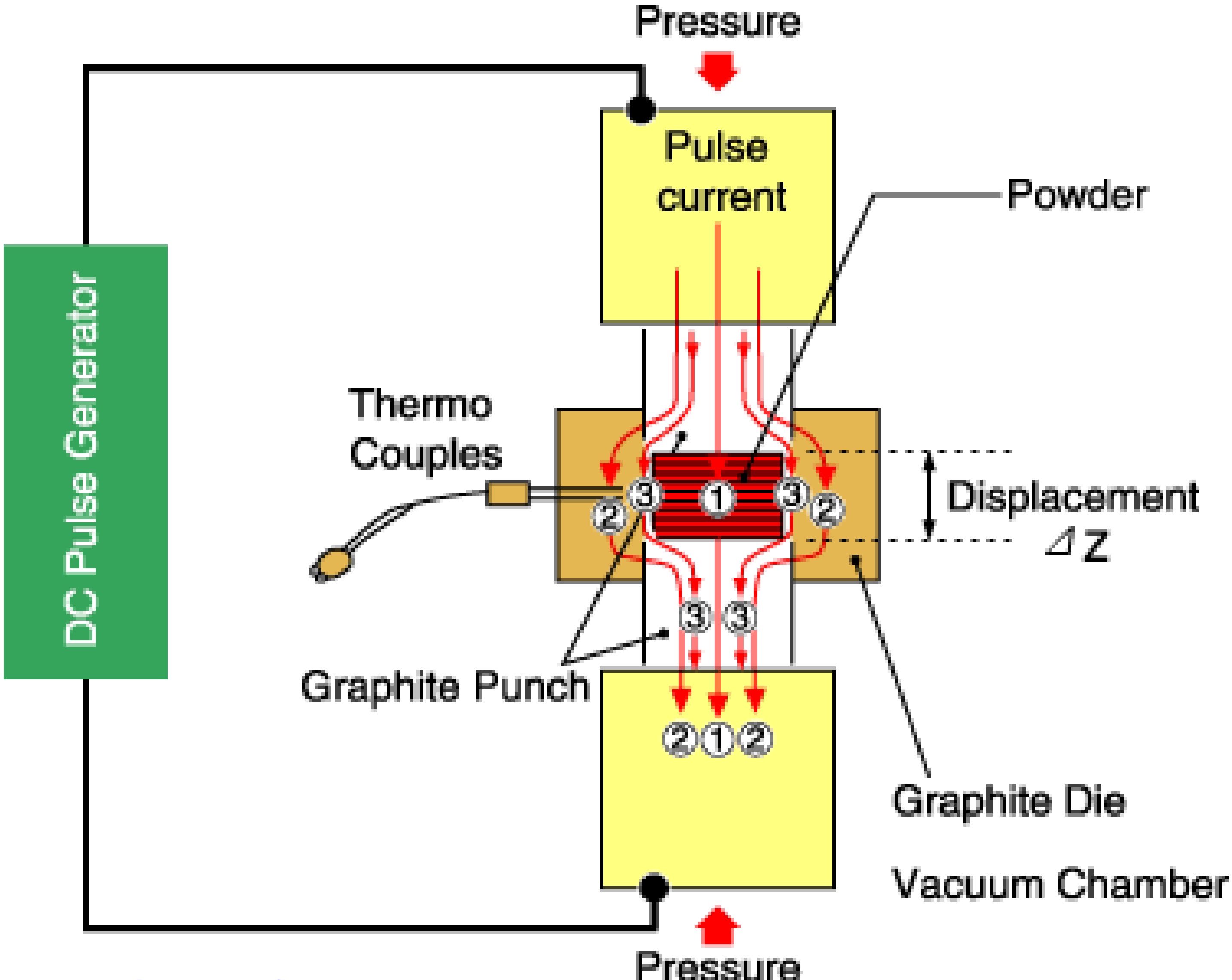
- **The surface activation results in clean grain boundaries. The grain boundary area shows direct grain-to-grain contact, which is attributed to the physical activation of powder particle surfaces during pulsed current application i.e. enhanced grain boundary diffusion process.**

Effect of pulsed DC

- Formation of capacitor banks at the surface insulating films.
- Generation of electrical discharges across the capacitors (might result in plasma).
- Discharges manifested by the presence of arc, aiding in material transport.
- Localized heating of powder surfaces.
- Breakdown of insulating films due to thermal and electrical breakdown.
- Enhanced diffusion (sintering) kinetics, clean interfaces and good grain to grain bonding.







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SPS effect

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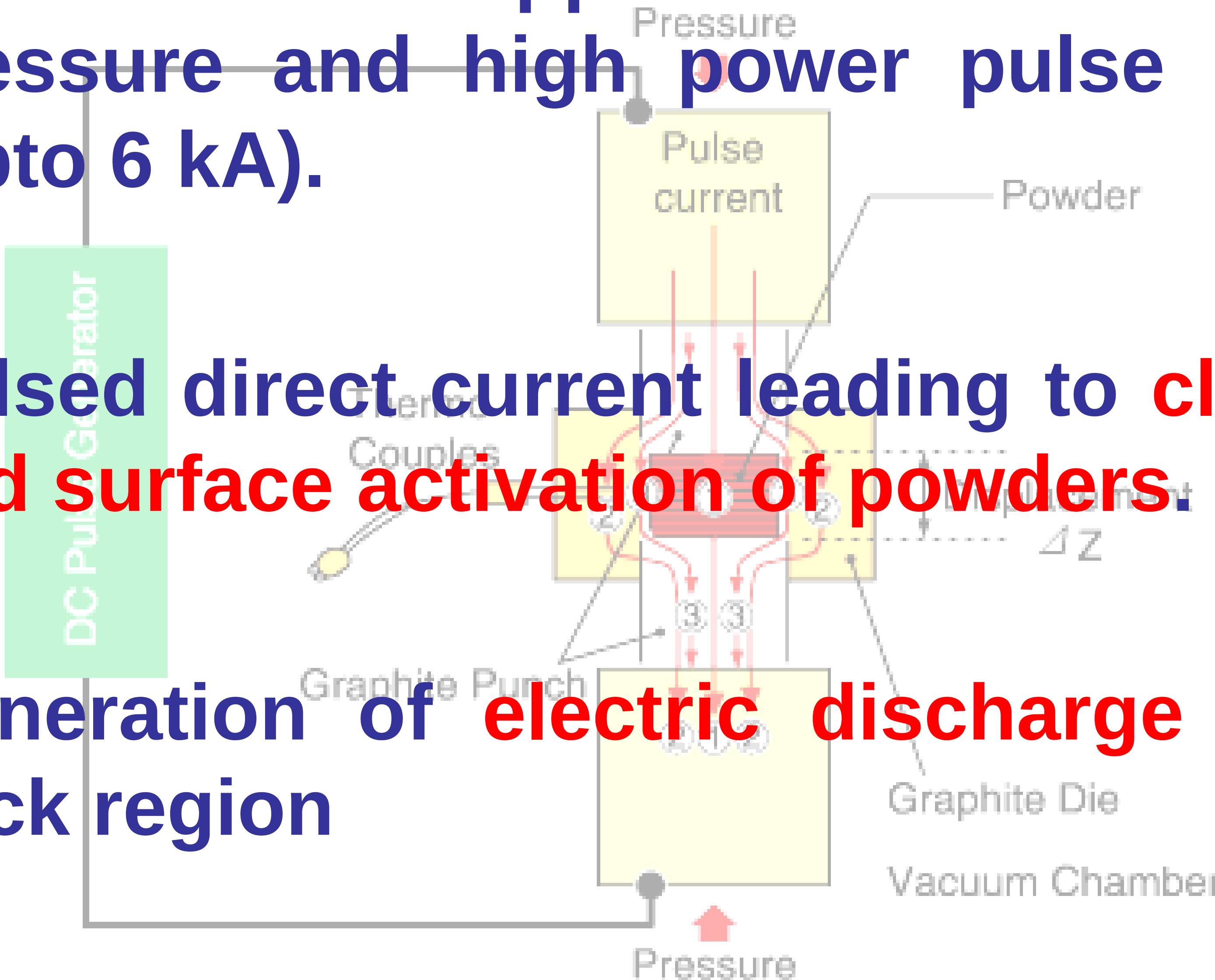


Simulation of Temperature Profiles in SPS

Fundamental heat transfer equation to solve:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\partial^2 T}{\partial \theta^2}+\dot{q}=\frac{1}{\alpha}\frac{\partial T}{\partial t}$$

Solution provides:

$$\frac{dT}{dr}=-\frac{\dot{q}_1}{2k_1} \quad \textbf{When} \quad 0\le r\le r_1$$

$$\frac{dT}{dr}=-\frac{\dot{q}_2}{2k_2}-\frac{r_1^{\,2}\ \ \dot{q}_1-\dot{q}_2}{2k_2}\frac{1}{r} \quad \text{When} \quad r_1\le r\le r_2$$

Devesh Tiwari, B. Basu and K. Biswas; Simulation of Thermal and Electric field Evolution during Spark Plasma Sintering; Ceramics International (2008)

Simulation of Temperature Profiles in SPS

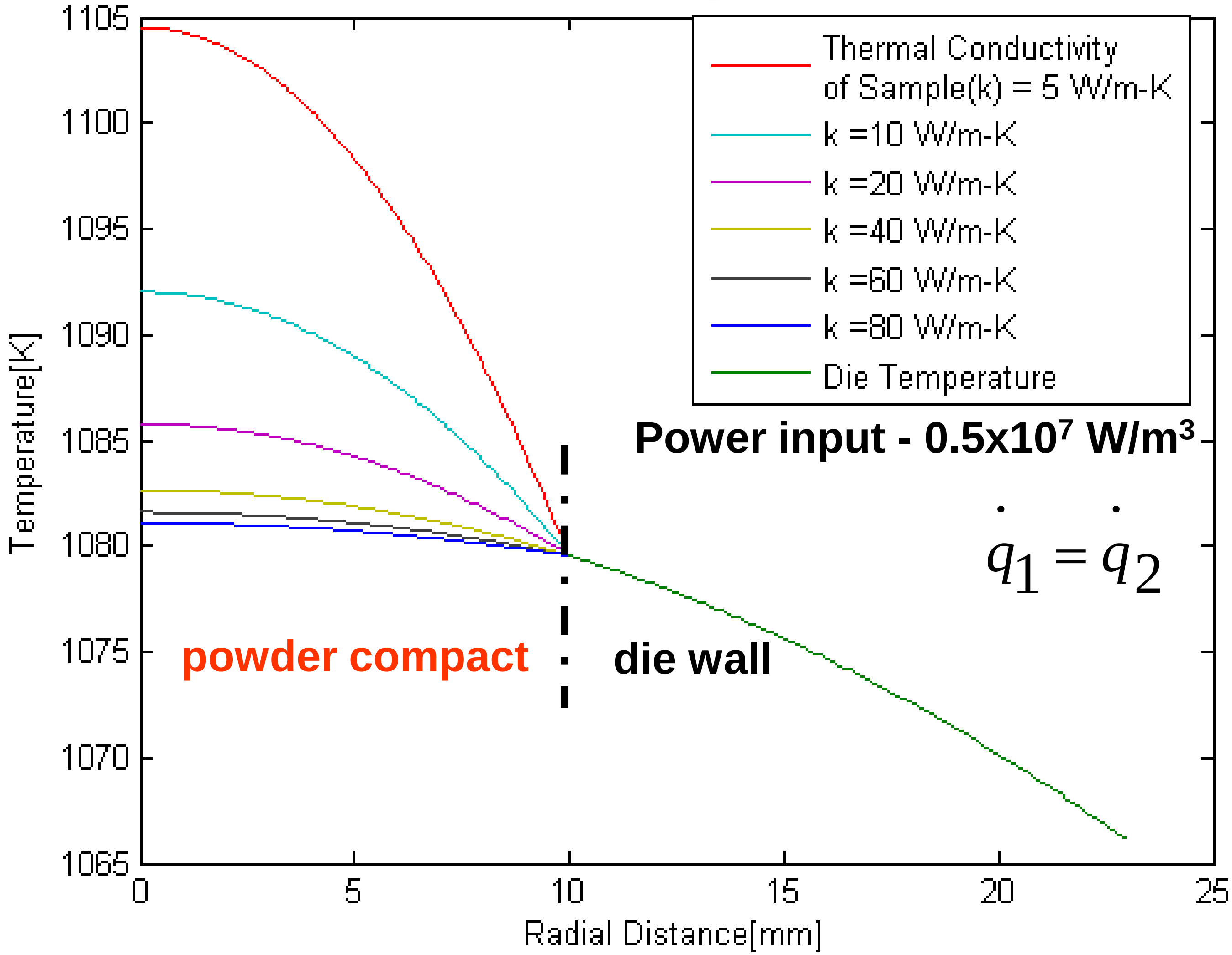
Surface temperature:

$$T_2 = \left\{ \frac{1}{2\varepsilon\sigma} \left[\dot{q}_2 r_2 + \frac{r_1^{\,2}}{r_2^{\,2}} \; \dot{q}_1 - \dot{q}_2 \; + T_\infty^4 \right] \right\}^{1/4}$$

ε = emissivity of graphite die

σ = Stefan-Boltzman Constant

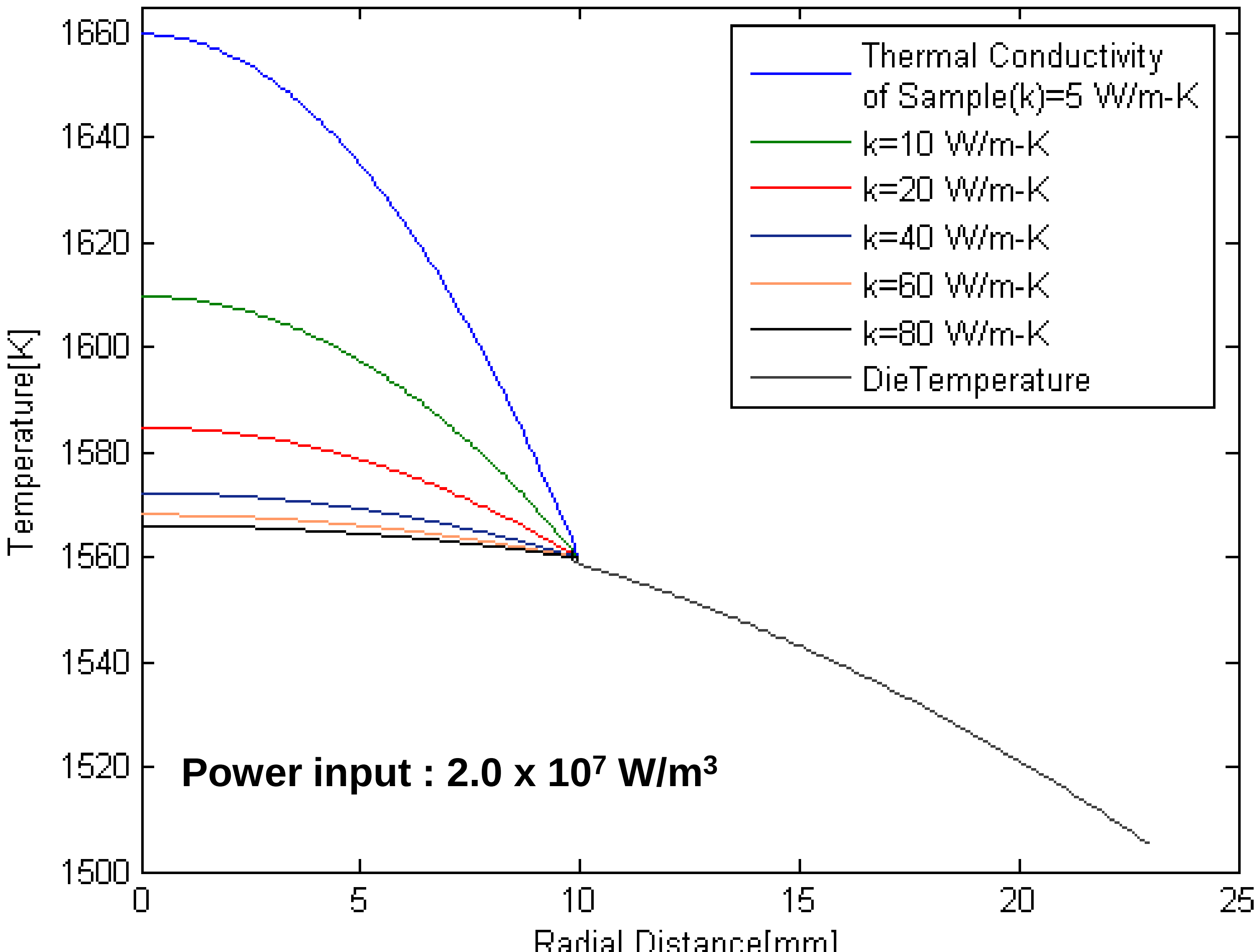
MATLAB Simulation of Temperature Profiles in SPS



- ❑ **Temperature gradient across powder compact strongly sensitive to both power input and thermal conductivity.**

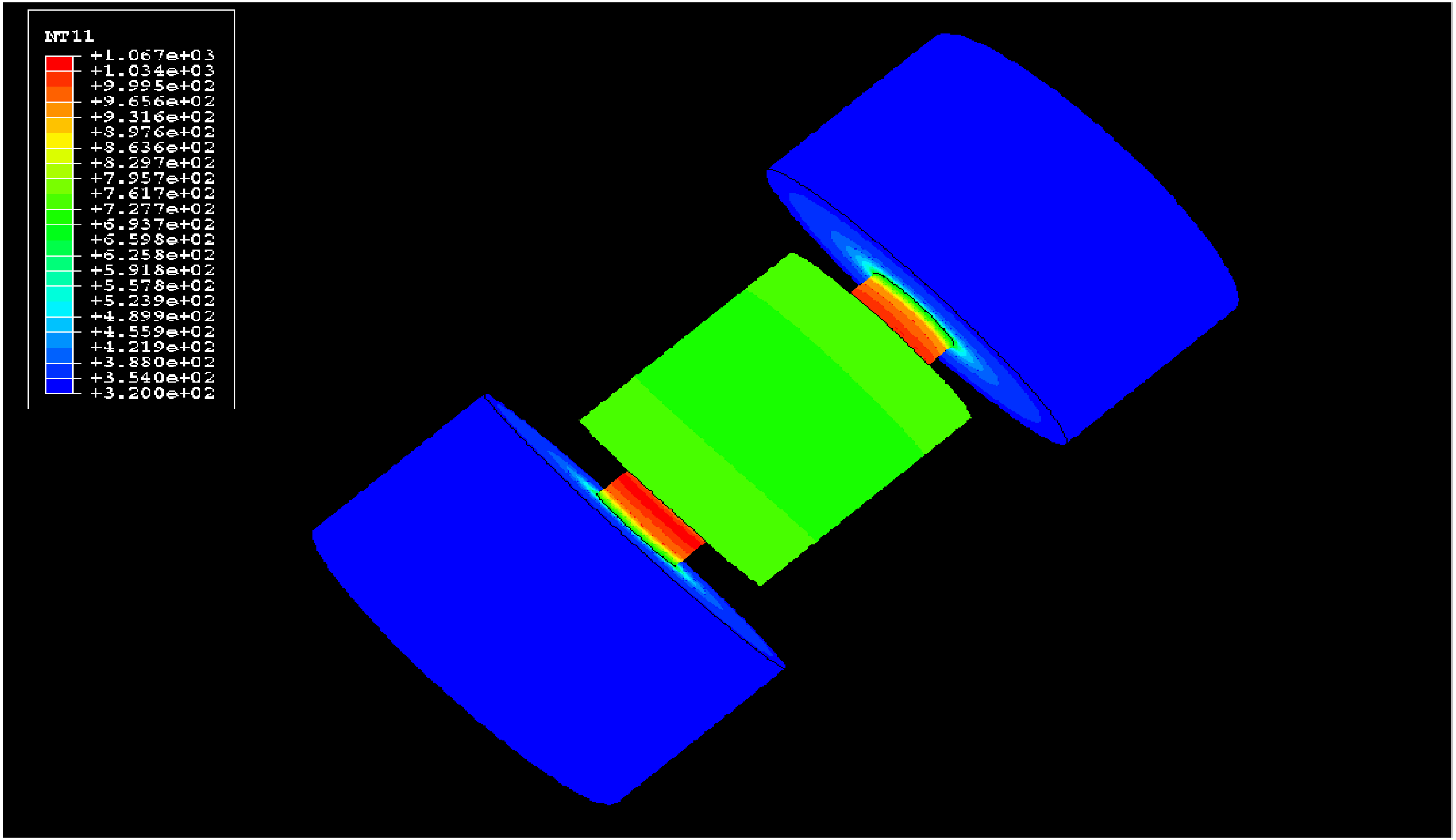
- ❑ **No significant difference in gradient observed for high thermal conductivity (40 W/m.K or above)**

MATLAB Simulation results (contd ..)



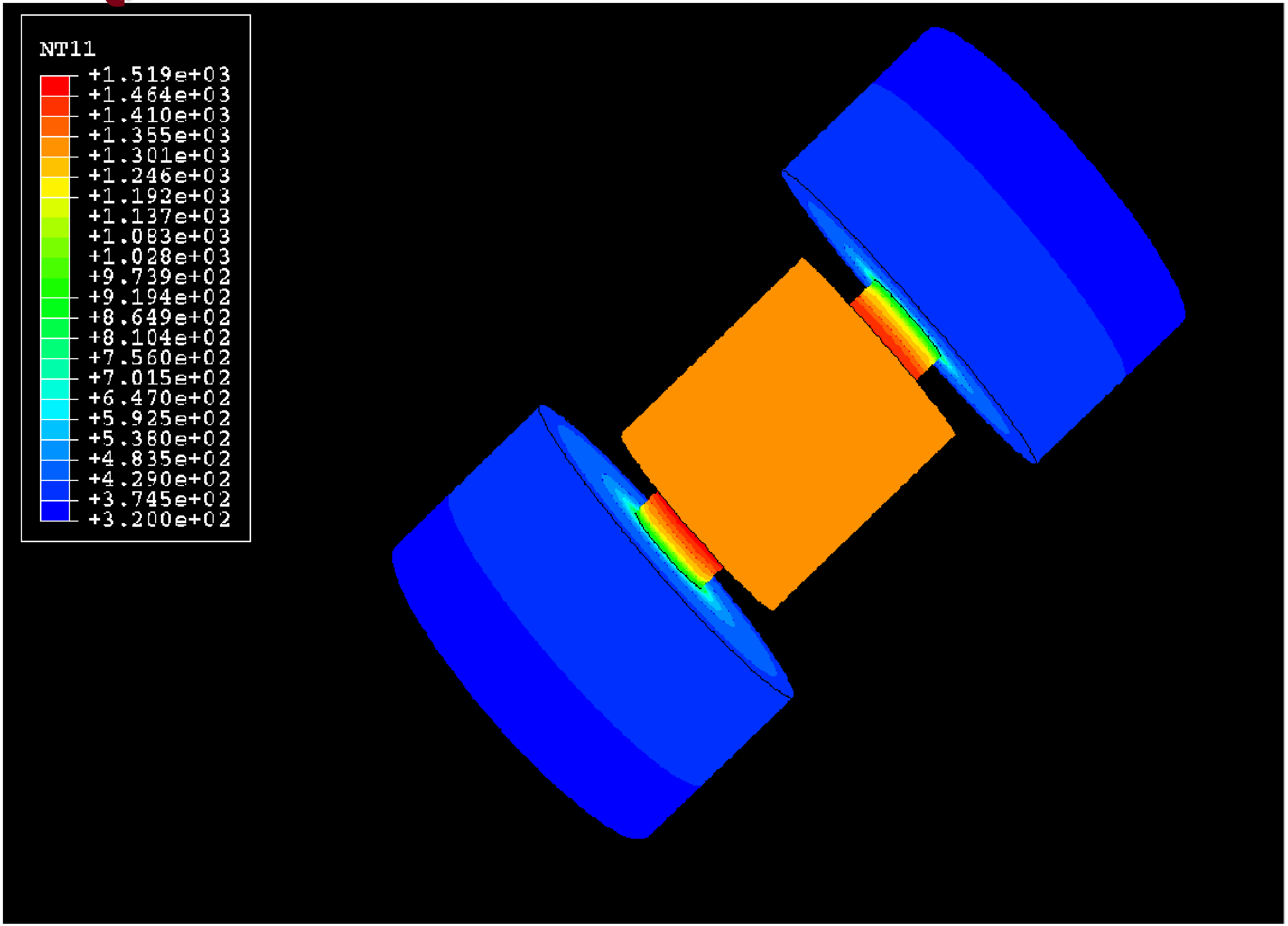
For lower thermal conductivity (20 W/m.K or less), the temperature gradient increases with power input level.

ABAQUS Simulation (Overall thermal conditions)



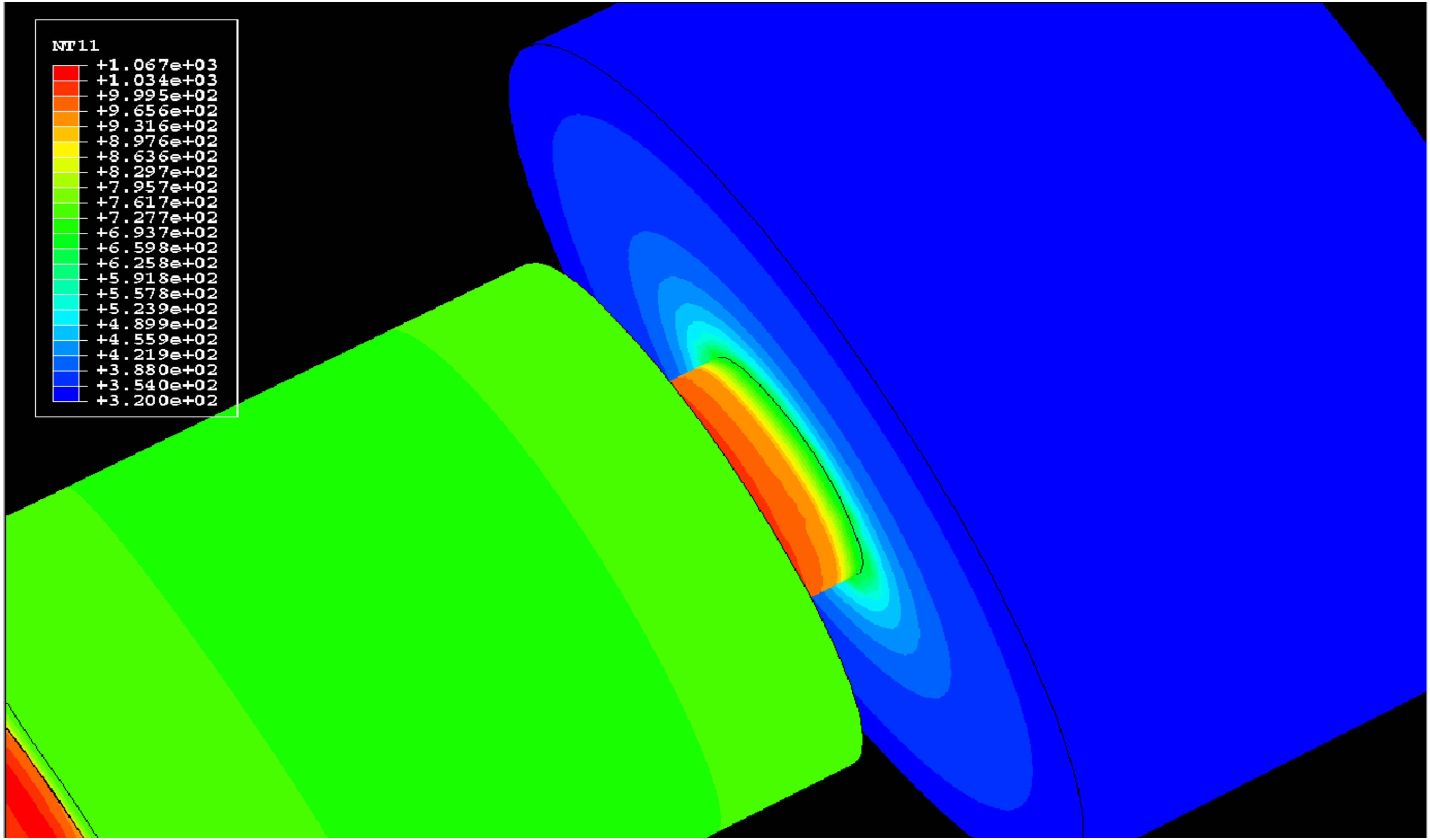
Power input - 1.25 x 10^7 W/m^3; holding time - 90 seconds

ABAQUS Simulation of Thermal effects in SPS



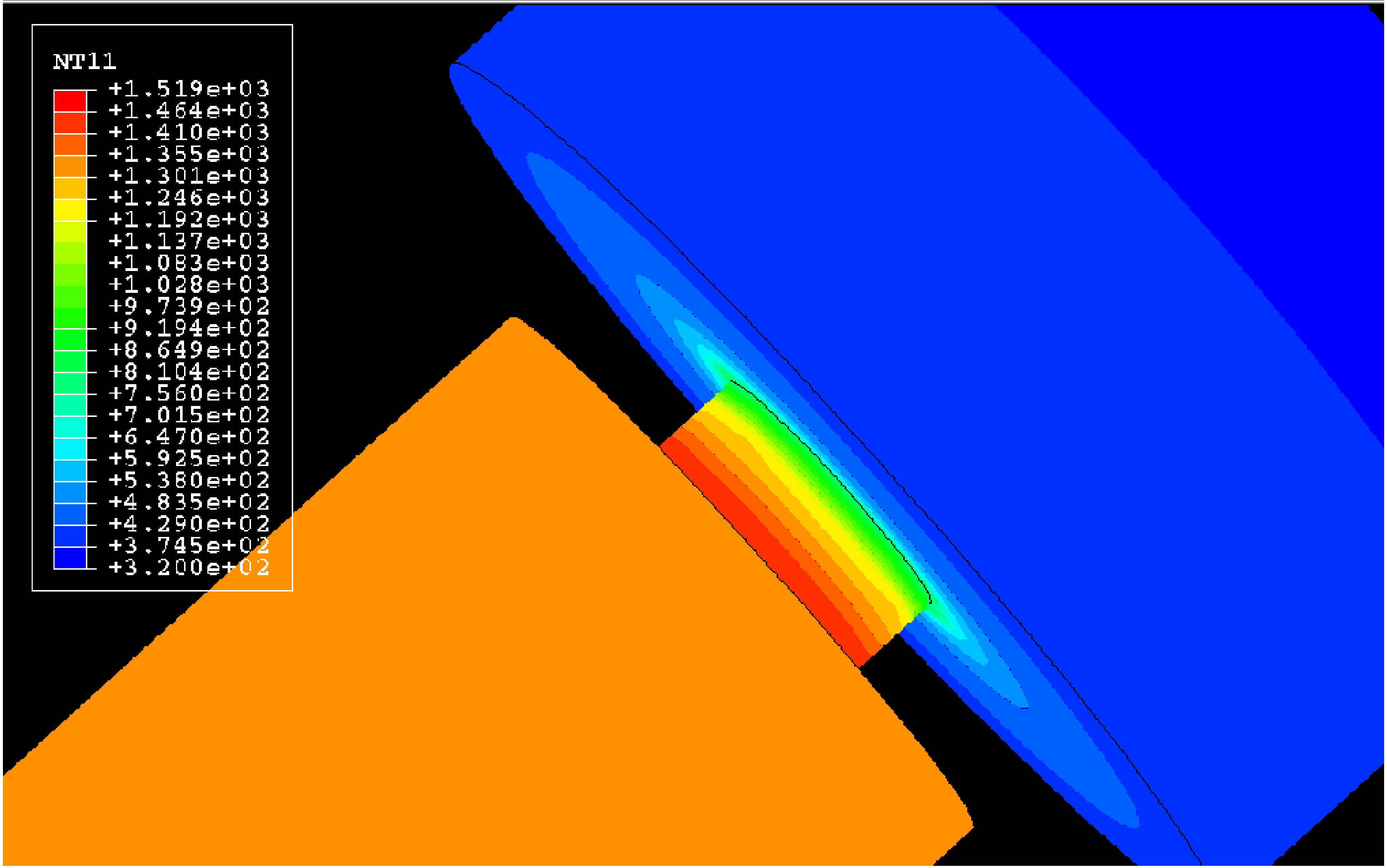
Power input - 1.25 x 10^7 W/m^3; holding time - 450 seconds

ABAQUS Simulation of thermal effect (closer view)



Power input - 1.25 x 10^7 W/m^3; holding time - 90 seconds

ABAQUS Simulation (closer view of punch/die)



Power input - 1.25 x 10^7 W/m^3; holding time - 450 seconds

Electrical Current Density and Heat Flux

Electrical Current Density, ECD

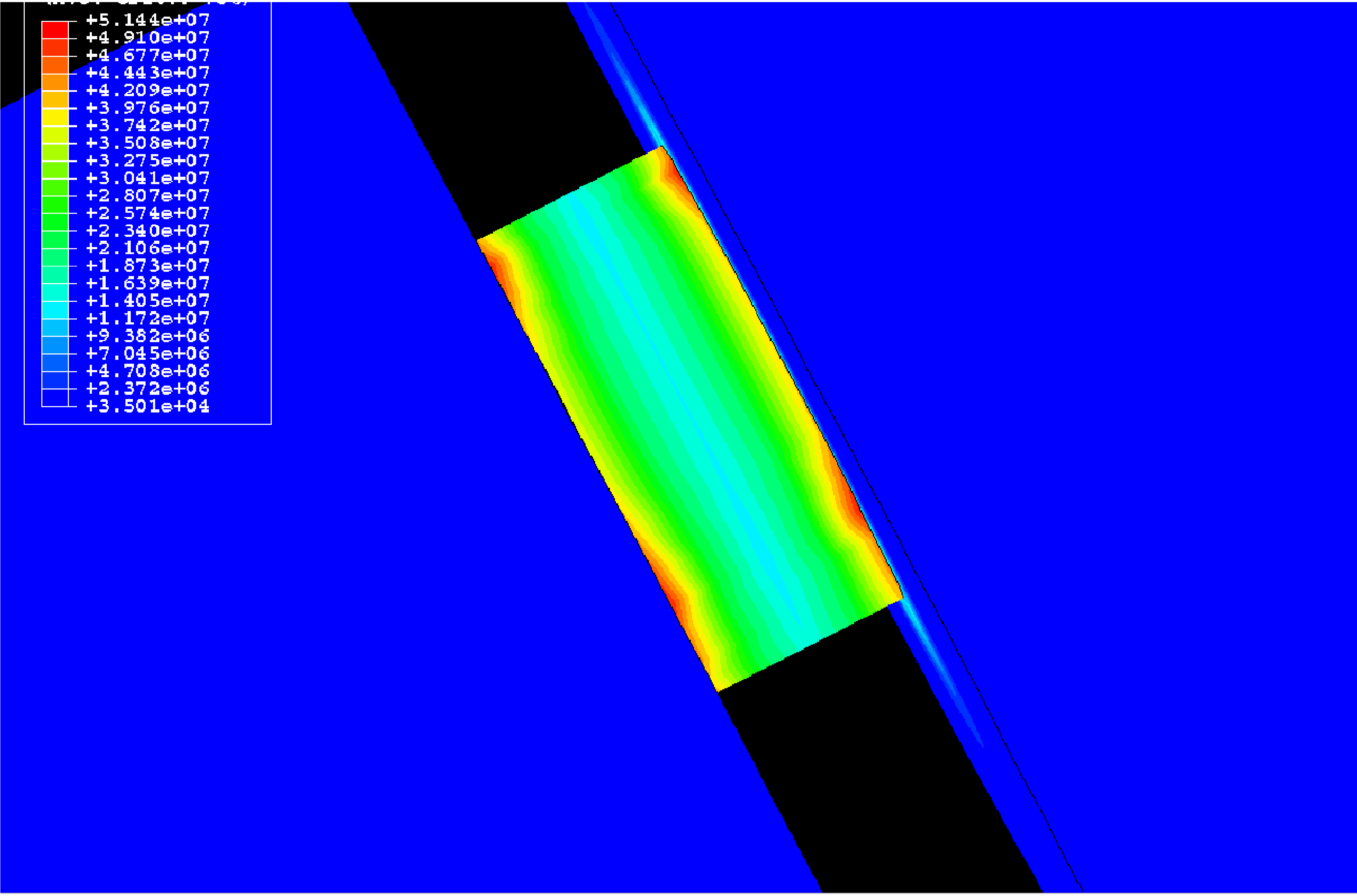
$$\vec{J} = ECC \times (V_2 - V_1)$$

Amount of heat flux, $\vec{q} = TCC \times (V_2 - V_1)$

$$ECC(T) \quad or \quad TCC(T) = \frac{\beta \exp\left(\frac{T - T_0}{T_L - T_0}\right)}{\alpha R_0 \ A_C}$$

ECC - electrical contact conductance ($\Omega^{-1}m^{-2}$),
TCC - thermal contact conductance ($W^{-1}m^{-2}K^{-1}$)
R_0 - static electrical (or thermal) contact resistance measured at reference temperature T_0,
A_C - contact area, α and β are empirical constants.

ABAQUS Simulation: ECD effect



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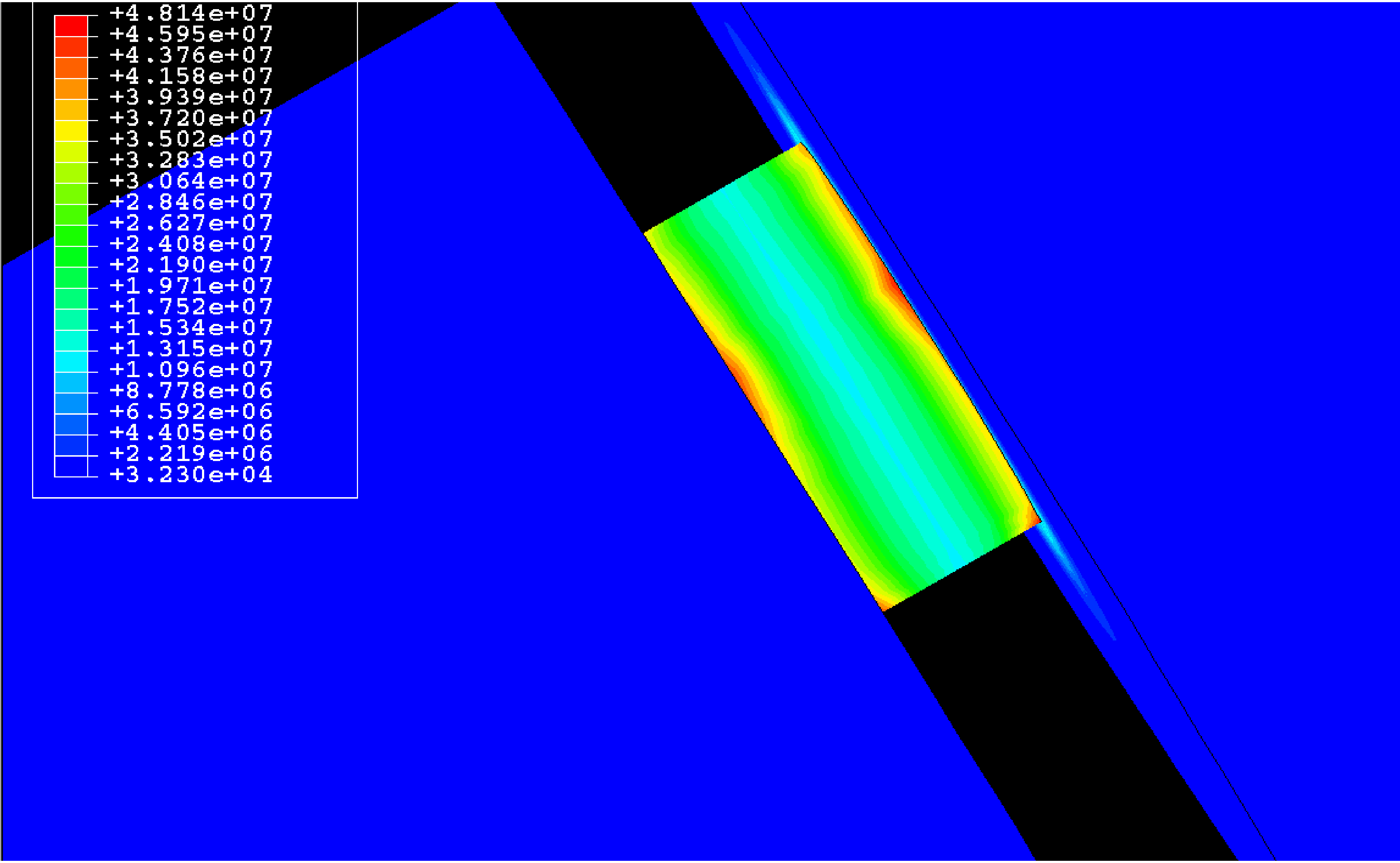
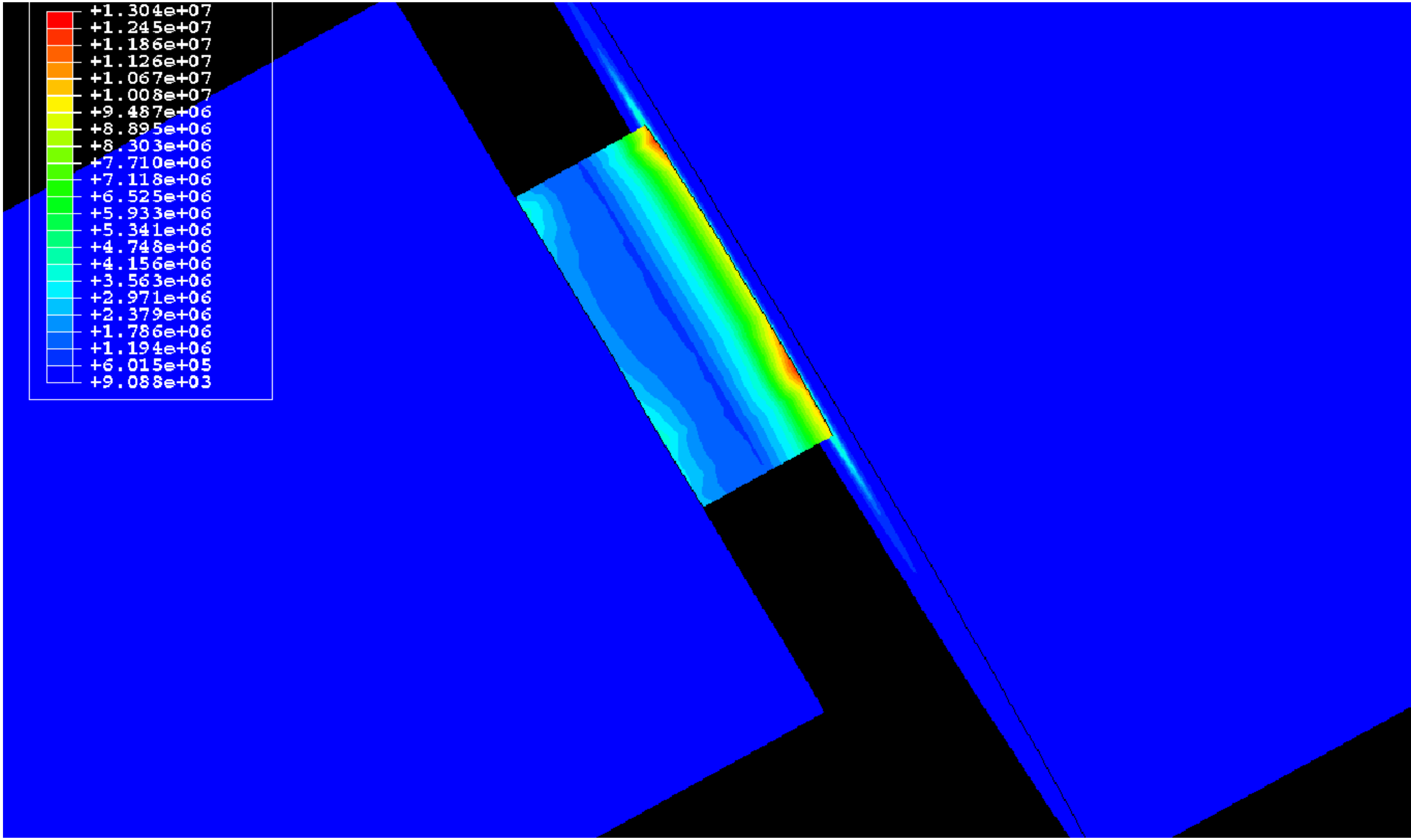
ABAQUS Simulation: ECD effect



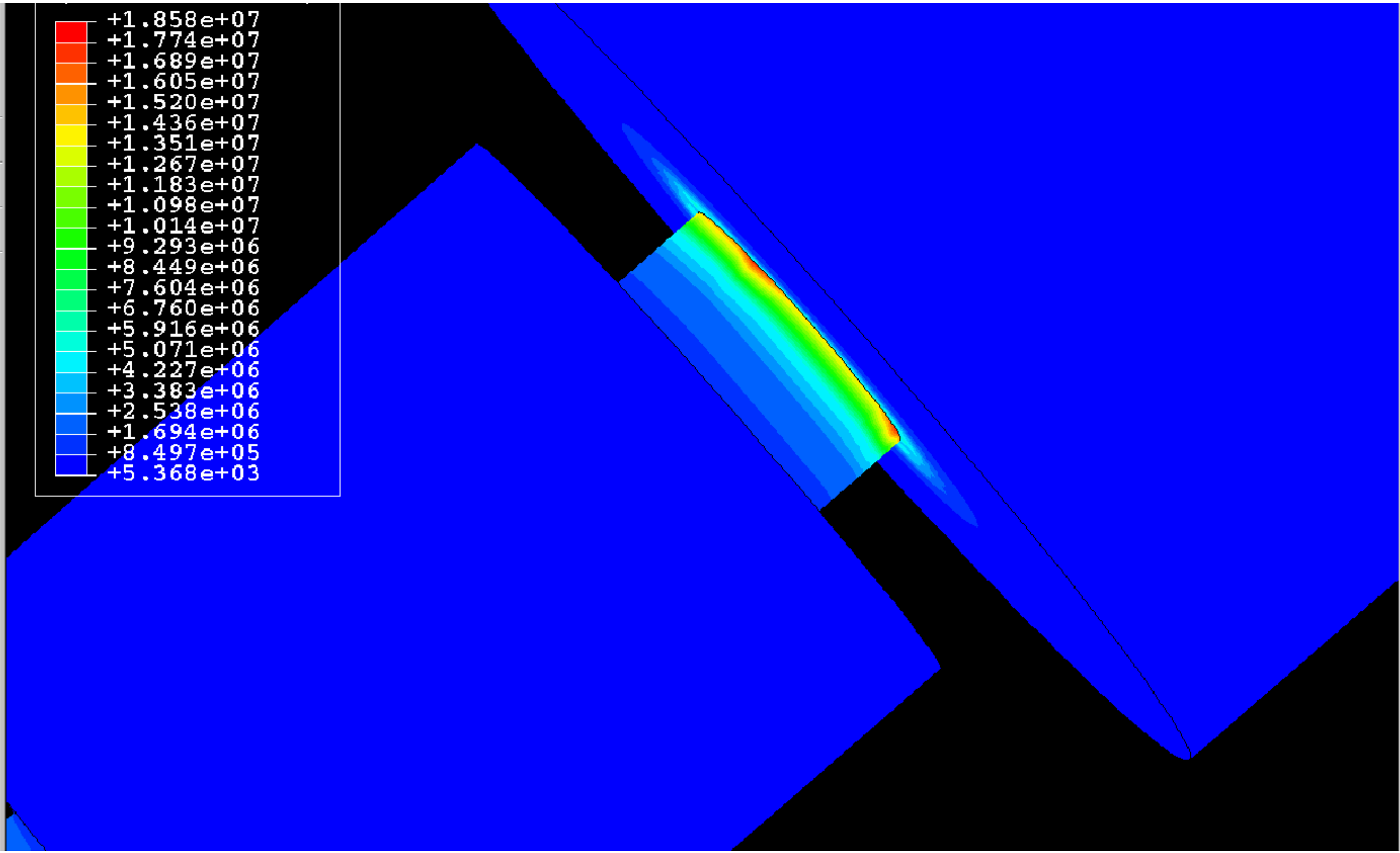
Power input - 1.25 x 10^7 W/m^3; holding time - 450 seconds

ABAQUS Simulation: Heat Flux Distribution effect



Power input - 1.25 x 10^7 W/m^3; holding time - 90 seconds

ABAQUS Simulation: Heat Flux Distribution effect



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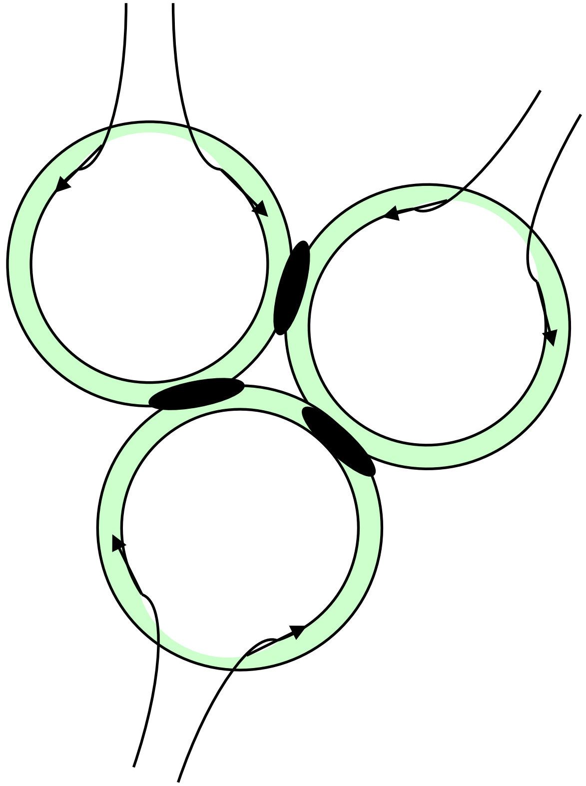
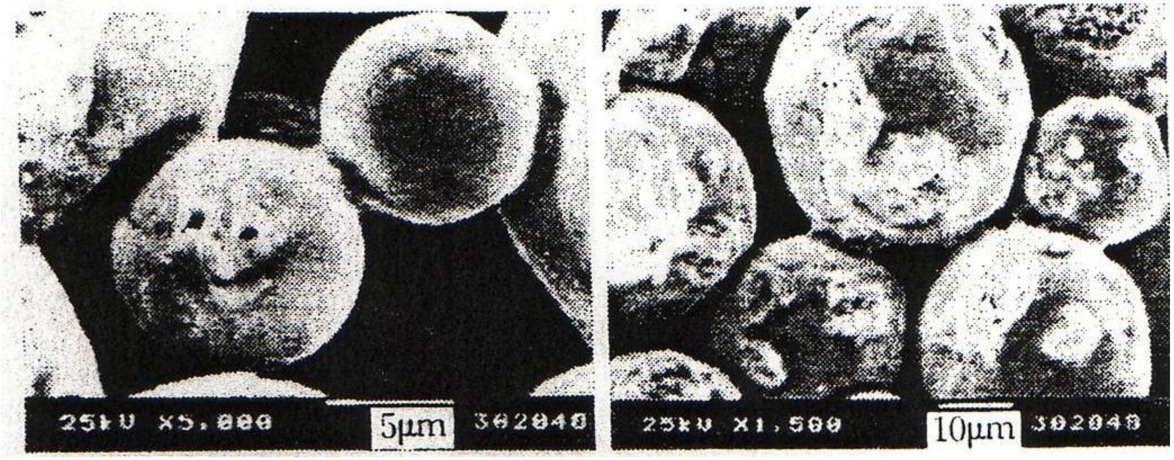


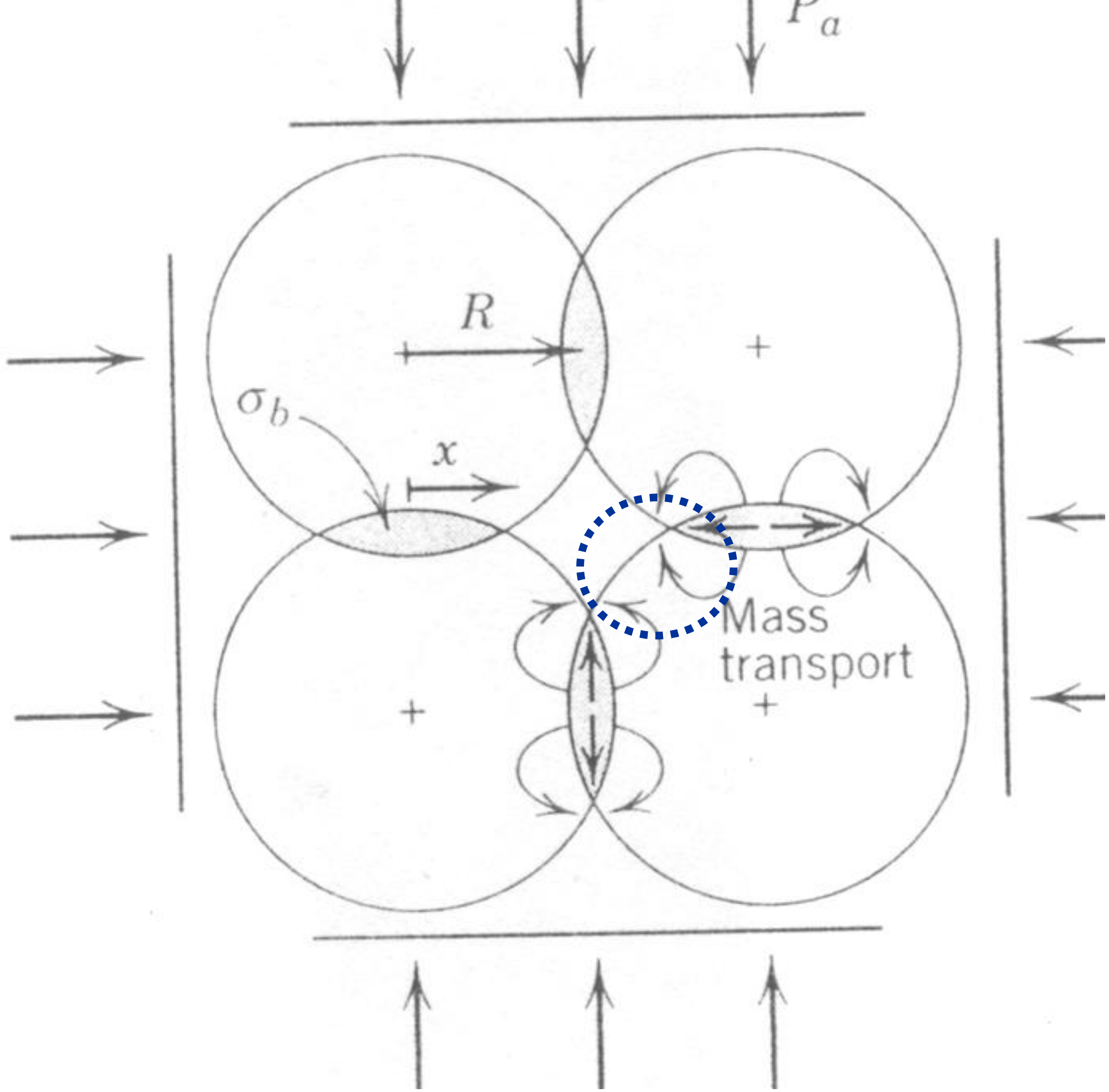
Joule's heating: localized temperature increment



Neck formation due to localized heating

Groza et al., UC Davis

In the presence of pressure and electric current, localized necking occurs faster due to joule heating. Consequently, the temperature raises very fast (faster than conventional sintering and Hot pressing) and the densification is completed within few minutes



❑ Because of faster heating rate, initial stage of sintering i.e. surface diffusion avoided

❑ Localized increase in temperature at particle/particle contact leads to faster mass transport process; D = f (T, ECD) under electric field

Experiments/Modeling for better understanding

An unified model required to explain the mechanisms of enhanced sintering during SPS process

$$\left(\frac{x}{r}\right)^6 = \left[\frac{192\delta\gamma D_b\Omega}{KT}\right]\frac{t}{r^4}$$

$$\left(\frac{x}{r}\right)^5 = \left[\frac{80\gamma D_l\Omega}{KT}\right]\frac{t}{r^3}$$

Modification of above neck growth equations considering electric field effect and temperature gradient during SPS