

19 mars 2015, 70 ans de la SF2M



HAUT-COMMISSAIRE
À L'ÉNERGIE ATOMIQUE

Matériaux de structure et propriétés fonctionnelles: du cahier des charges au matériau sur mesure

Yves BRECHET

**Grenoble-INP / SIMAP / CEMAM
Haut Commissaire à l'Énergie Atomique**

R.Dendievel, L.Cecilia S.Gorsse, T.Pardoen

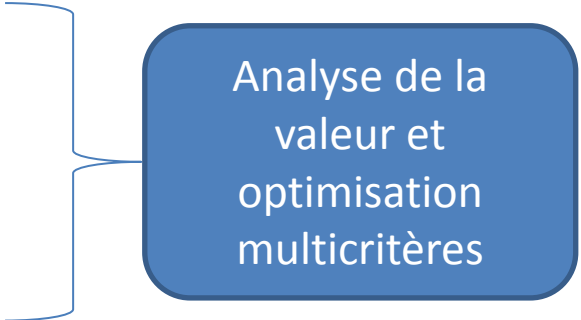
Quelques notions de sélection des matériaux

- Astreintes : rigidité, solidité,
- Objectifs: masse, volume, prix...
- Variables géométriques imposées



Indices de Performance

- Problèmes multi-astreinte
- Problèmes multi-objectifs



Analyse de la valeur et optimisation multicritères

Quelques remarques pragmatiques

- Toute application pratique est nécessairement la résultante d'un compromis
- La tendance naturelle des chercheurs est de se focaliser sur la propriété la plus séduisante
- Les matériaux qui ont un futur industriel sont plutôt ceux qui présentent un **compromis** de propriétés attractif
- Très souvent on demande des propriétés **contradictoires** : l'art de la science des matériaux est de « Remplir les trous dans l'espace des matériaux »

Plan de l'exposé

- Il n'y a pas que la limite d'élasticité dans la vie
 - Absorption d'énergie
- Matériaux multifonctionnels: la stratégie de la microstructure
 - Les thermoélectriques
 - Les conducteurs à haute tenue mécanique
- Matériaux multifonctionnels: la stratégie de l'architecture
 - Les brûleurs radiants
 - Les matériaux isolants ablatifs

**Il n'y a pas que la limite
d'élasticité dans la vie...**

Absorber l'énergie d'un choc

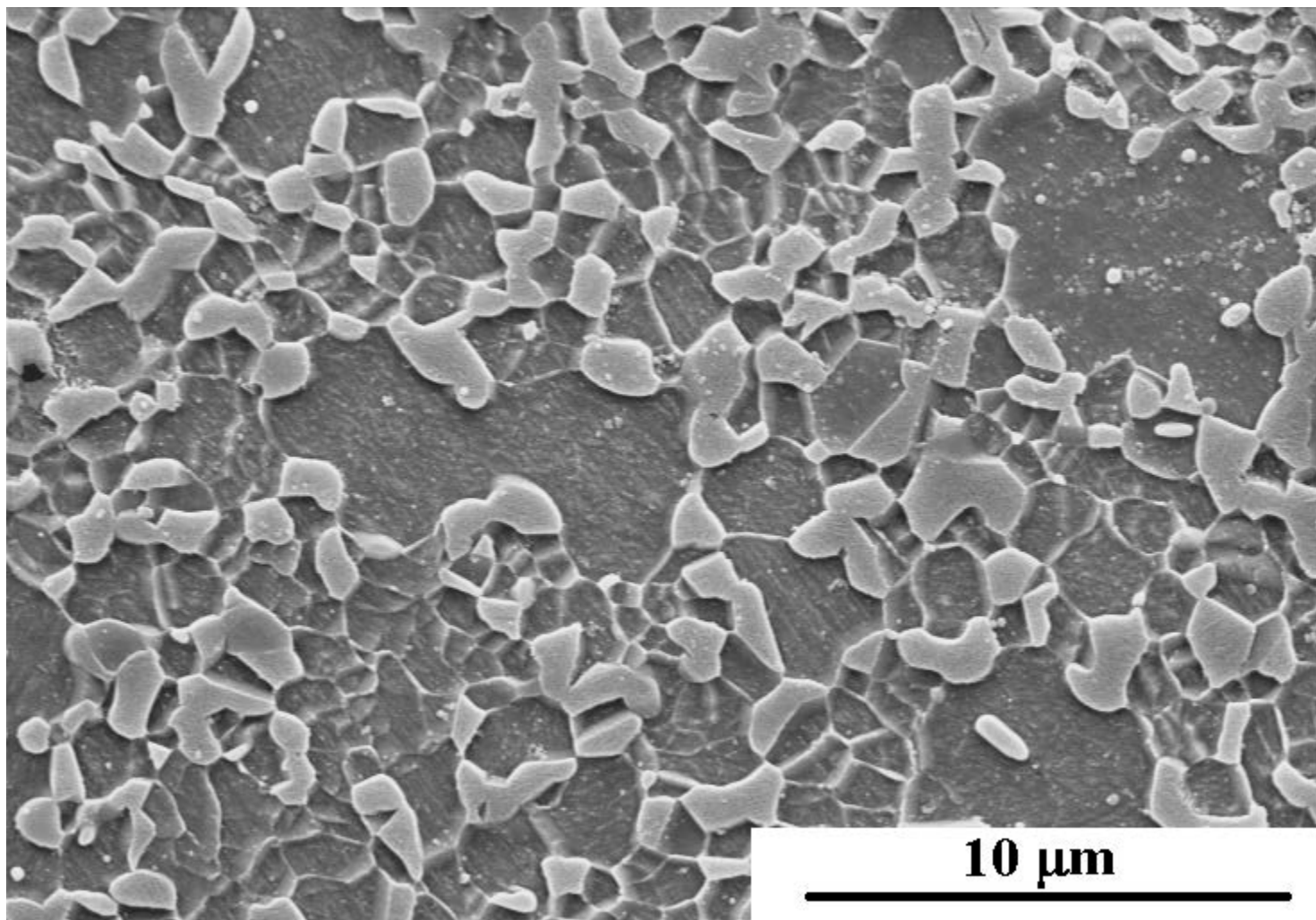
Les aciers Dual Phase

- Aciers avec des îlots de martensite (issus de la trempe de l'austénite) dans une matrice de ferrite polycristalline
- La ferrite se déforme plastiquement
- La martensite est élastique / fragile

⇒ « Composite Naturel »

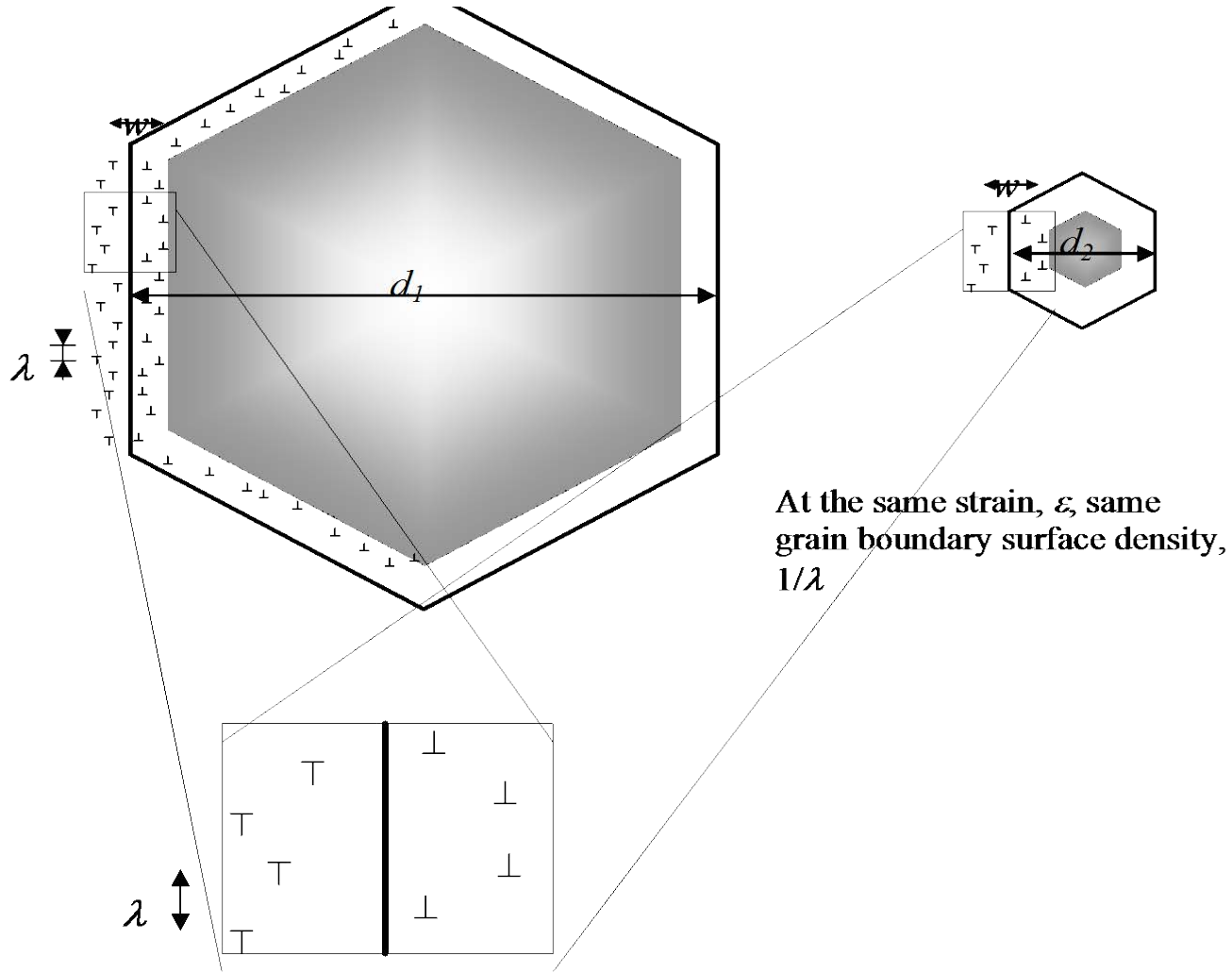
- Suivant les traitements thermomécaniques on peut faire varier la fraction volumique de martensite et la taille des grains de ferrite
- On recherche à la fois une limite d'élasticité élevée et une ductilité importante (absorption d'énergie)

⇒ « Matériau sur mesure? »



10 μm

Schéma des dislocations au voisinage du joint de grain



Comportement de la ferrite dans un acier dual phase

Loi d'écoulement

$$\sigma_f = \underbrace{\sigma_{00}}_{\text{friction}} + \underbrace{\frac{k_{HP}}{\sqrt{d}}}_{\text{Hall-Petch}} + \underbrace{M\alpha\mu b\sqrt{\rho}}_{\text{Taylor}} + \underbrace{\frac{M^* \mu b}{2\pi \lambda} \left(1 - \underbrace{\left(1 - \frac{w}{d_f} \right)}_{\text{efficiency of screening}} \right)}_{\text{grain boundary hardening}} \frac{\lambda^*}{\lambda}$$

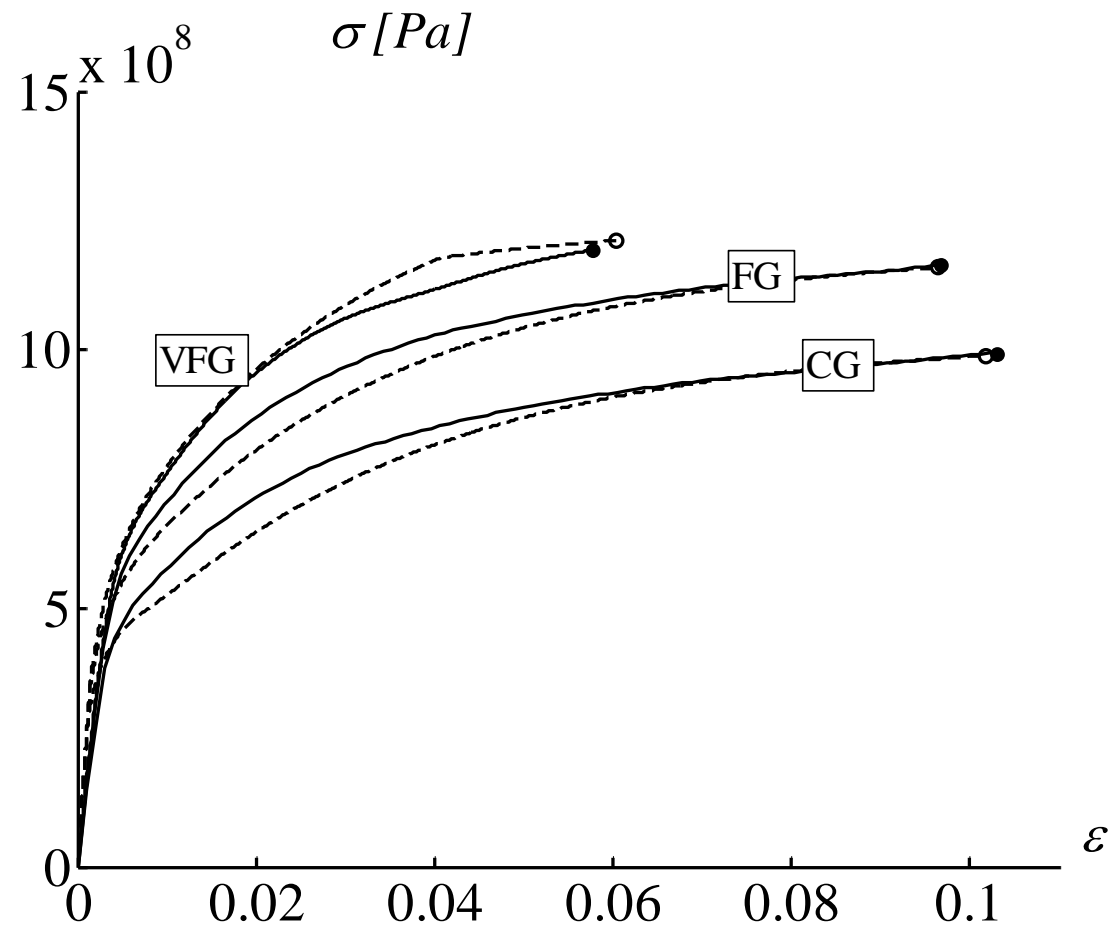
évolution des dislocations intergranulaires

$$\frac{d\rho}{d\varepsilon^p} = M \left(k_1 \sqrt{\rho} - k_2 \rho + \frac{k_3}{d_f} \frac{1}{b} \left(1 - \frac{\lambda^*}{\lambda} \right) \right)$$

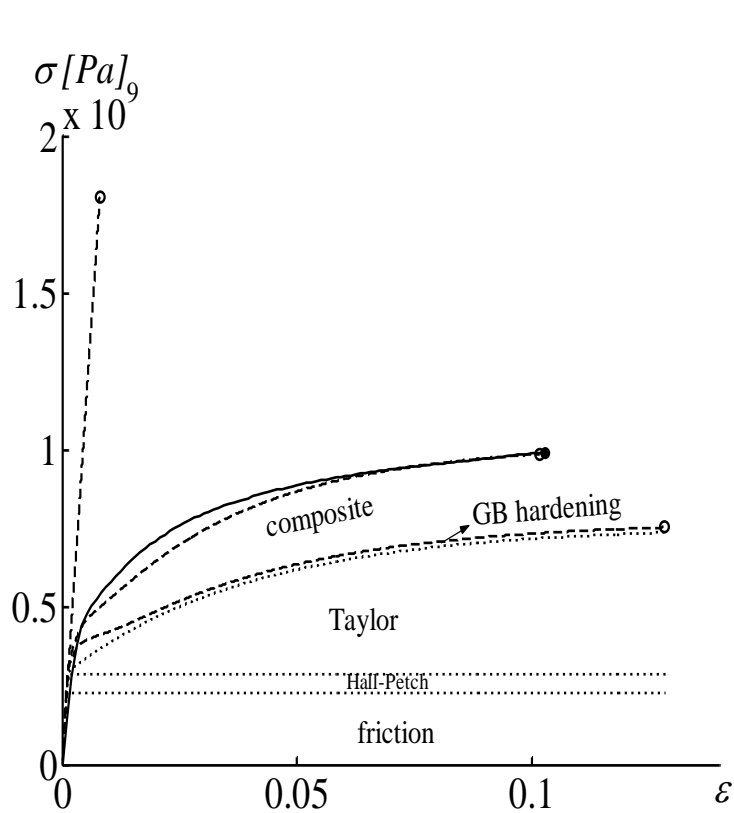
évolution des dislocations aux joints de grains

$$\frac{1}{\lambda} = \frac{1}{\lambda^*} \left[1 - \exp\left(\frac{-\lambda^* M \varepsilon^p}{b} \right) \right]$$

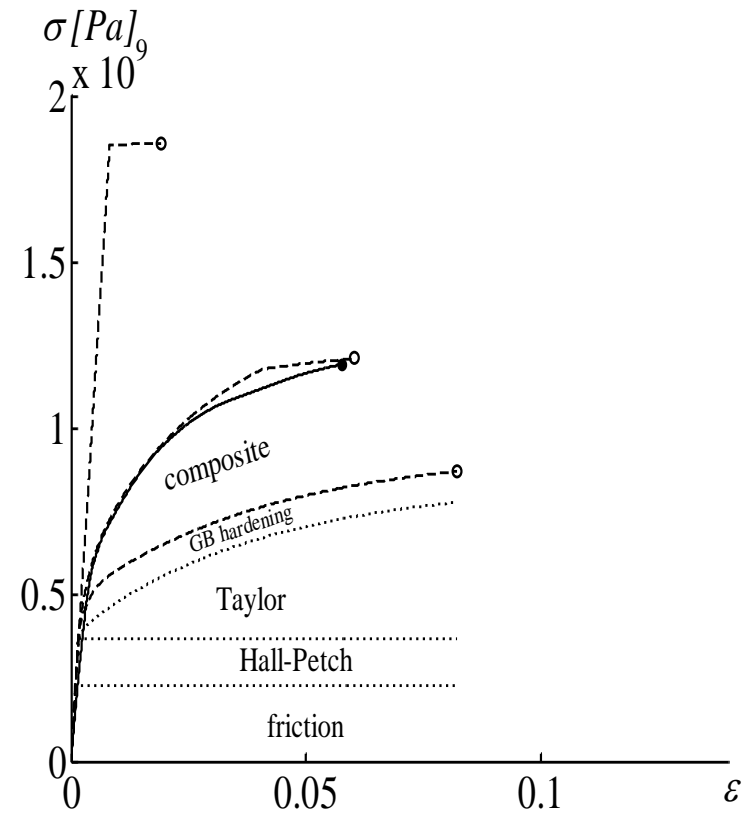
Modèle autocohérent de type Mori Tanaka avec des inclusions martensitiques élastiques



Contribution des différents termes à l'écrouissage

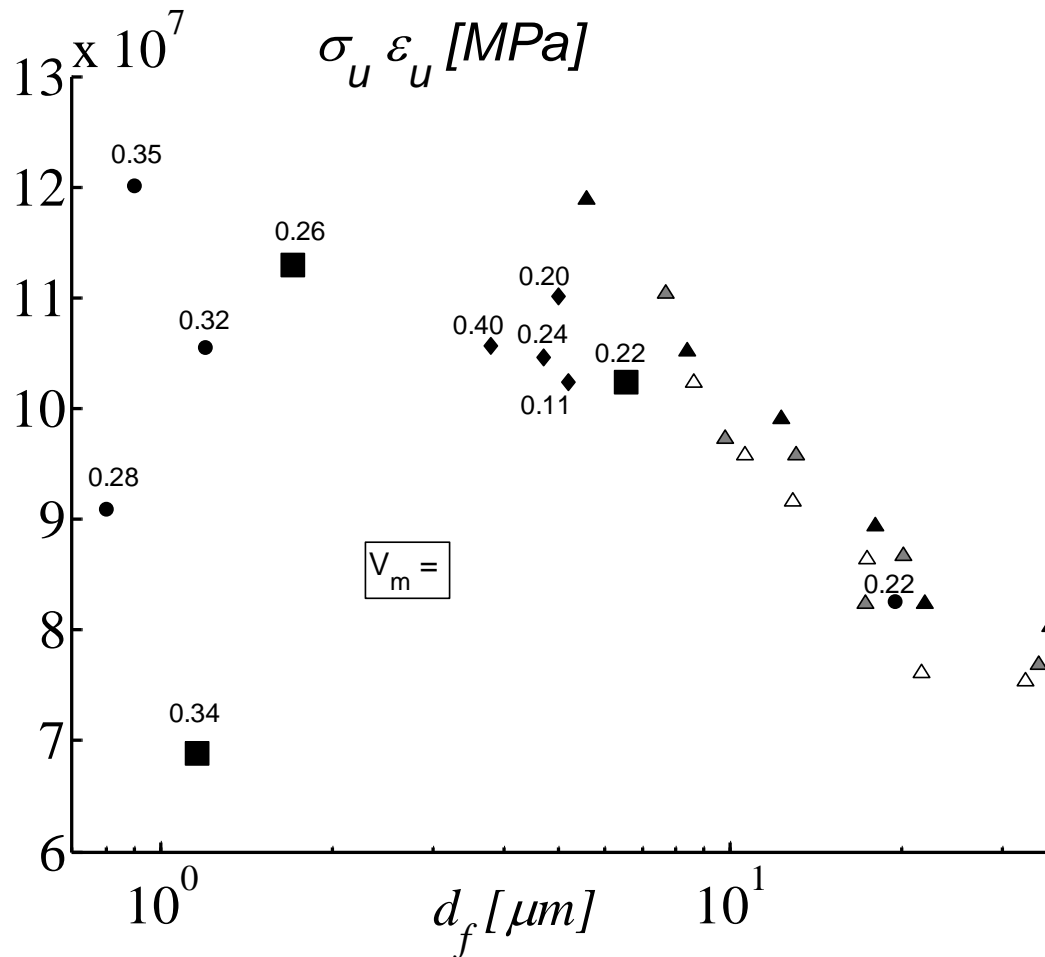


Ferrite à gros grains

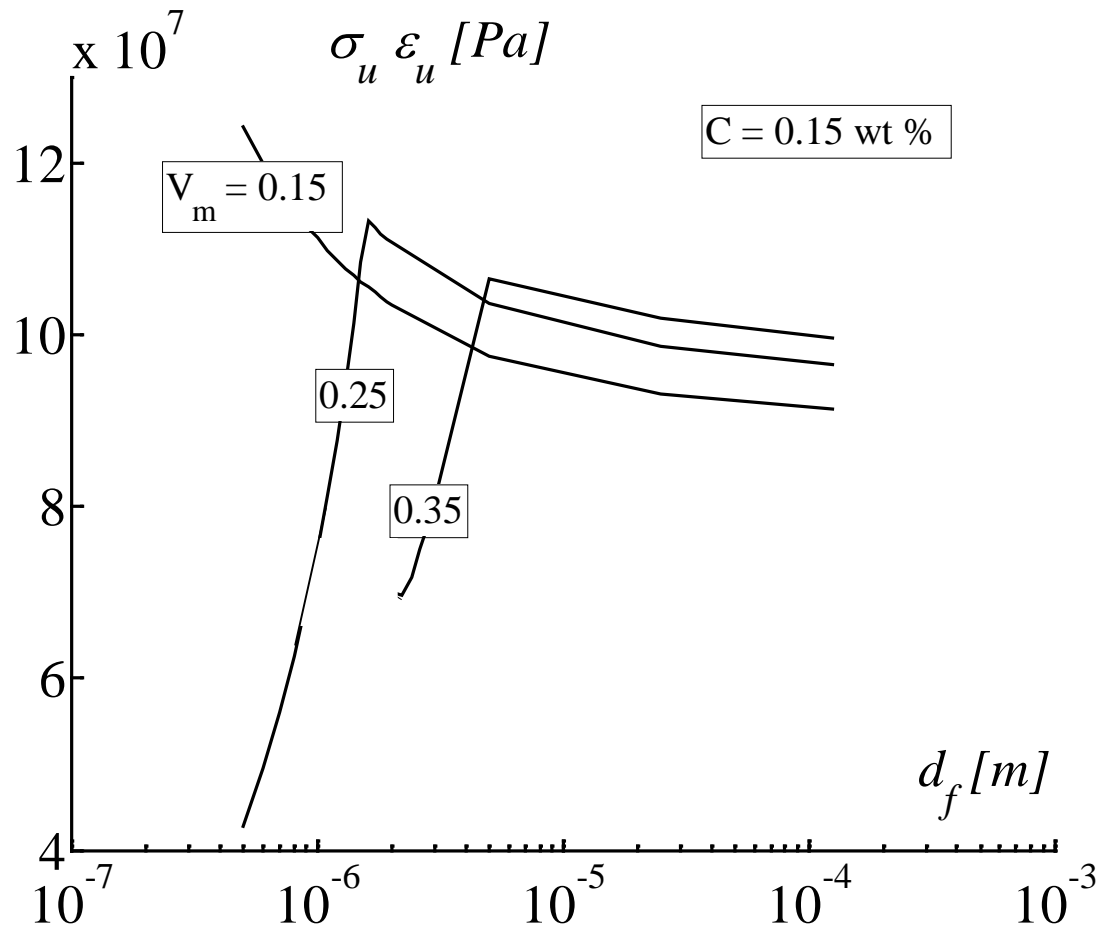


Ferrite à petits grains

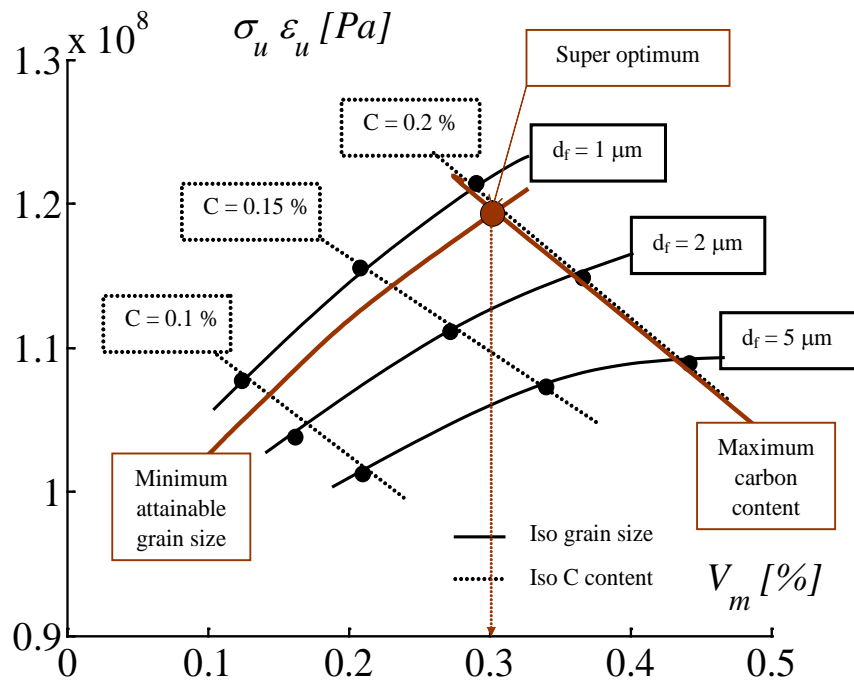
Données Expérimentales sur les aciers DP



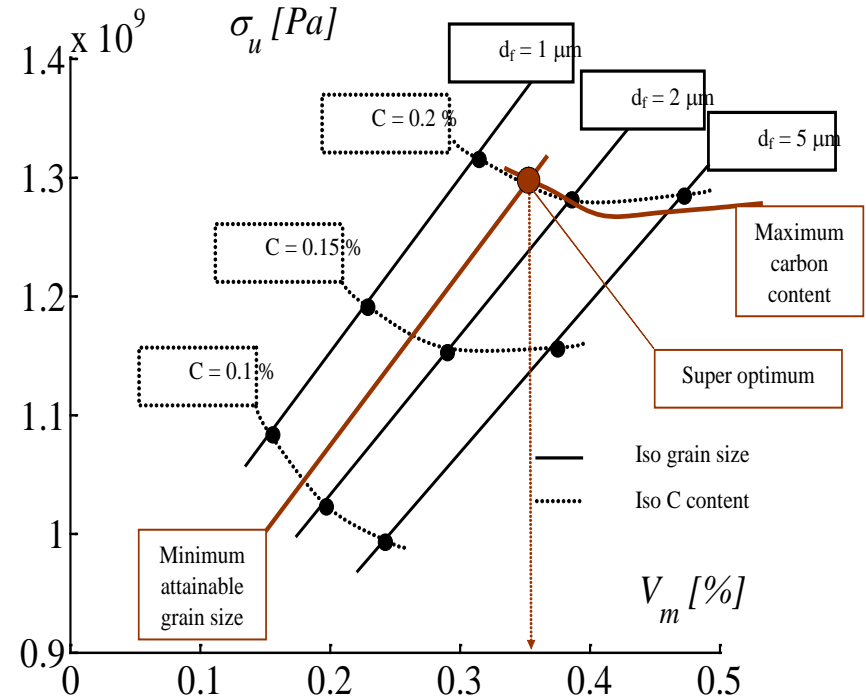
Optimum dans la taille de ferrite



Optimisation multicritère sur plusieurs paramètres microstructuraux



Absorption d'énergie maximale



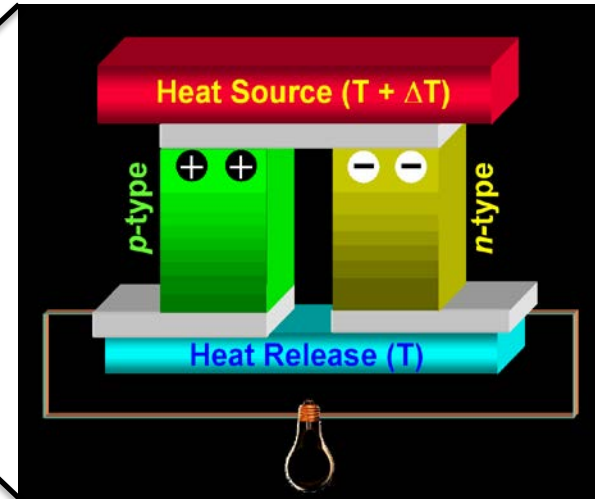
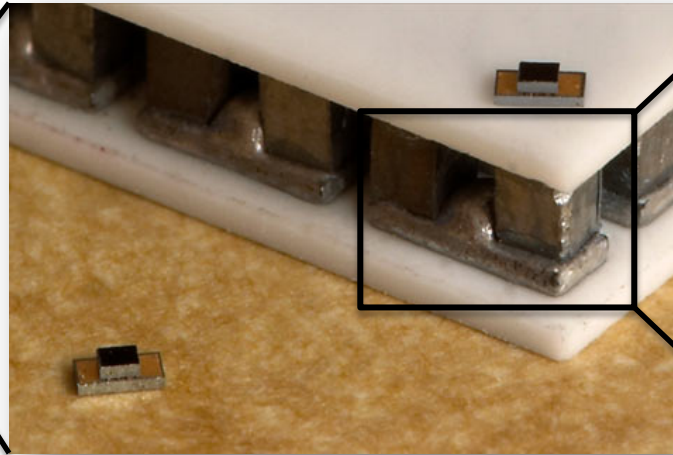
Astreinte de résistance maximale
avec une ductilité d'au moins 8%

Astreintes Procédés: taille minimale de ferrite, teneur maximale de C (soudage)

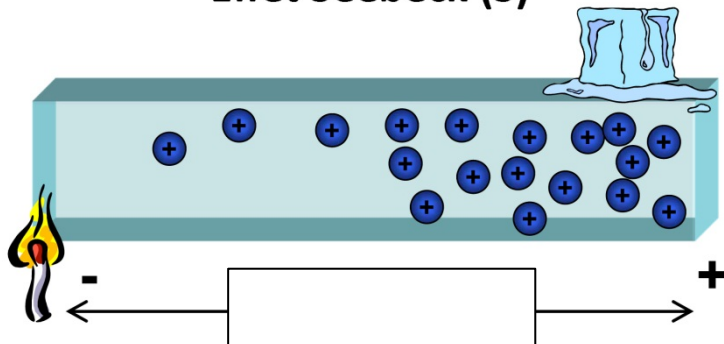
La stratégie de la microstructure
dans les matériaux fonctionnels...

***Les thermoélectriques: dialogue
avec les chimistes des solides***

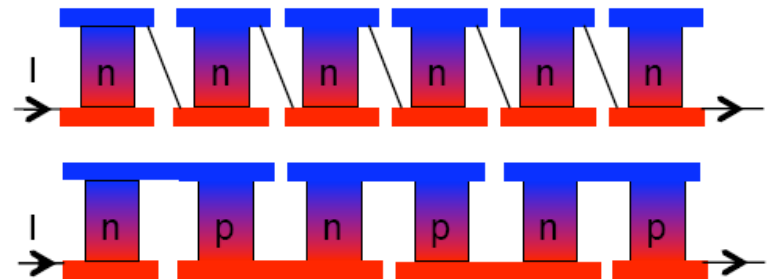
Thermoélectricité - Principe



Effet Seebeck (S)



Association parallèle / série



$$U \propto NS\Delta T$$

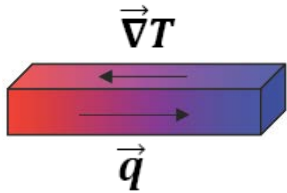
$$P \propto N\sigma S^2\Delta T^2$$

Thermoélectricité – Indice de performance

Efficacité de conversion :

$$\eta = \frac{P_u}{Q_c} = \frac{R_c I^2}{\underbrace{\kappa \Delta T}_{\text{Conduction}} - \underbrace{\pi I}_{\text{Effet Peltier}} - \underbrace{\frac{1}{2} R I^2}_{\text{Effet Joule}}}$$

Conduction

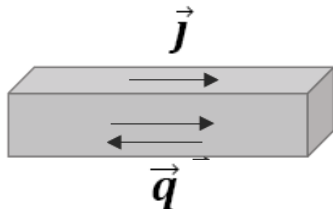


$$\vec{q} = -\lambda \vec{\nabla T}$$

Effet Joule

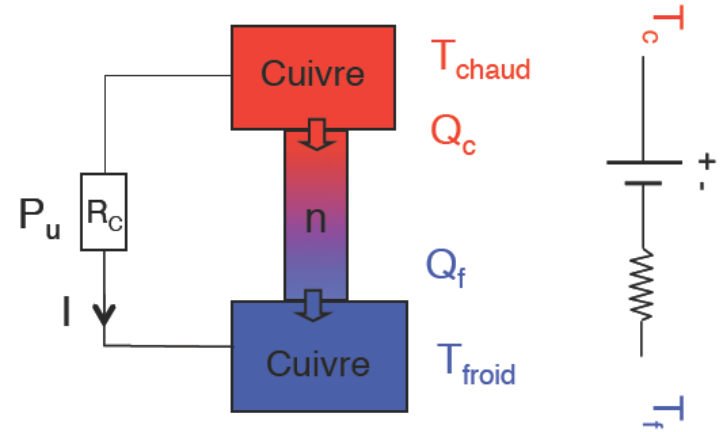


Effet Peltier



$$\vec{q} = \pi \vec{j} \quad \text{avec} \quad \pi = ST$$

Génération d'électricité (effet Seebeck)



optimisation de η : $\left(\frac{\partial \eta}{\partial R_c}\right) = 0$

$$\eta_{max} = \frac{T_c - T_f}{T_c} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_c}{T_f}}$$

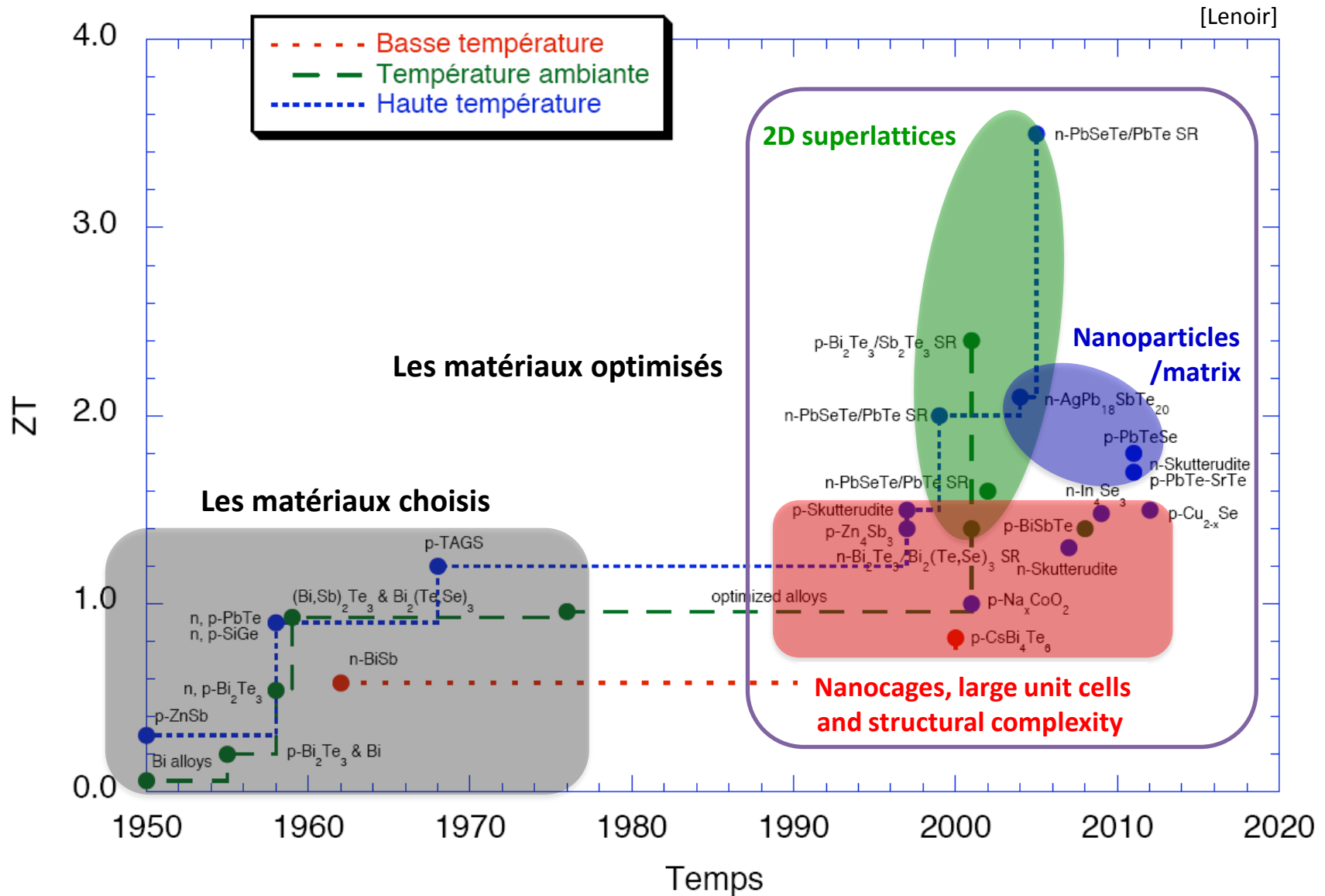
Coefficient Seebeck ($\mu\text{V/K}$) $\rightarrow S$

Conductivité électrique (S/m) $\rightarrow \sigma$

Conductivité thermique (W/mK) $\rightarrow \kappa$

$$ZT = \frac{S^2 \sigma}{\kappa}$$

Thermoélectricité – Des matériaux choisis aux matériaux optimisés



Thermoélectricité – Matériaux choisis

Matériau idéal :

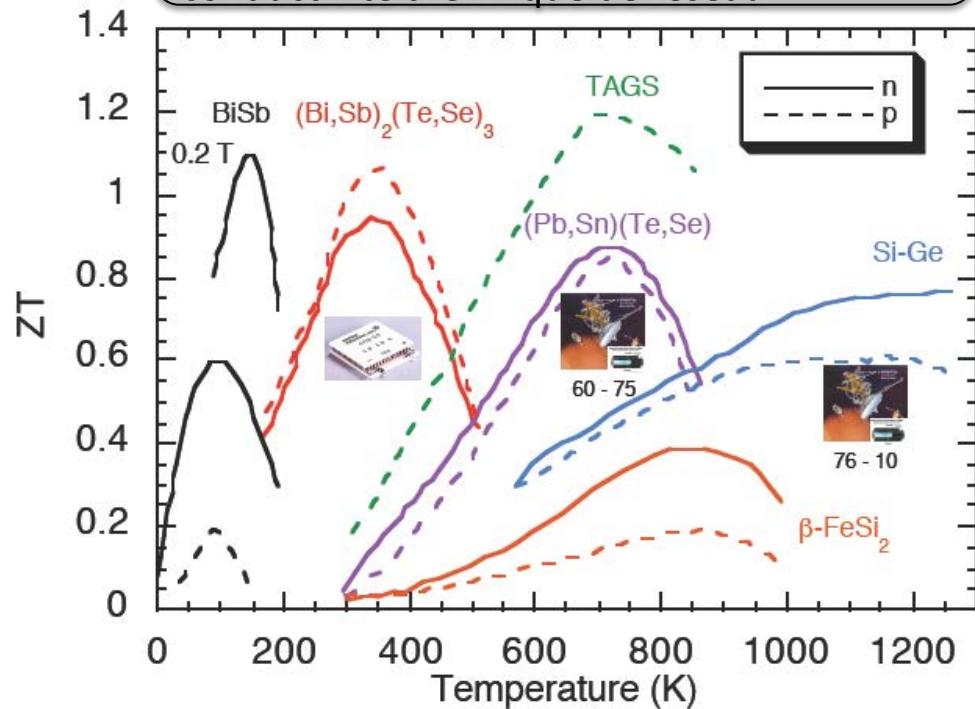
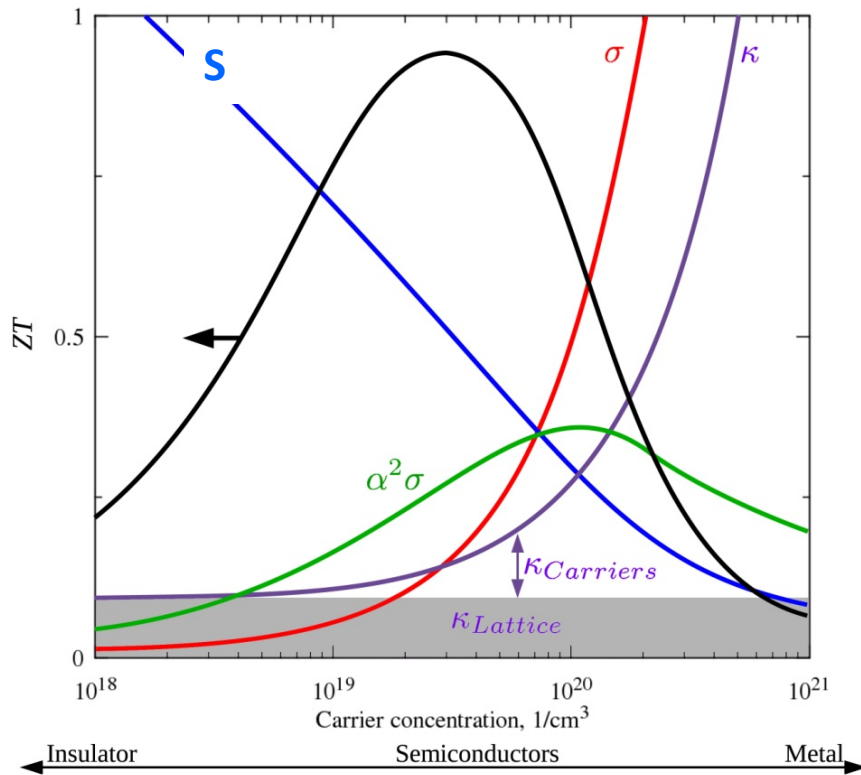
grd S , grd σ and faible κ

mais qd S augmente \rightarrow σ diminue

et qd σ augmente \rightarrow S diminue et κ augmente

Meilleur compromis :

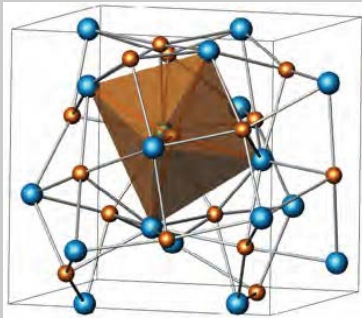
semiconducteurs avec une faible conductivité thermique de réseau



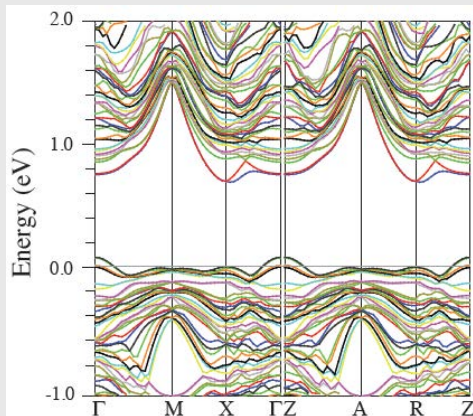
Les matériaux thermoélectriques : de l'importance de la microstructure

Indice de performance (facteur de mérite) : $ZT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2}{L_0} \left(1 + \frac{\kappa_{ph}}{\kappa_{el}} \right)^{-1}$

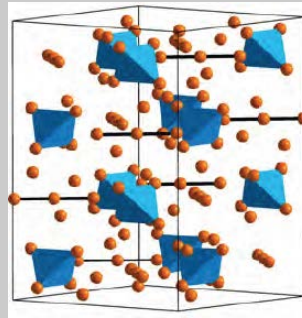
Physique du solide



Structure de bandes



Chimie du solide



Maille géante, cages

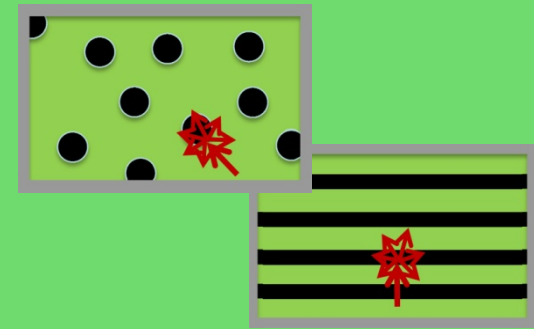
- multiplication des phonons optiques (peu contributifs au transport de chaleur)

- peu de phonons acoustiques

$$\kappa_{ph} = \frac{k_B v \lambda_{ph}}{V}$$

Science des matériaux et métallurgie

Composites PbTe



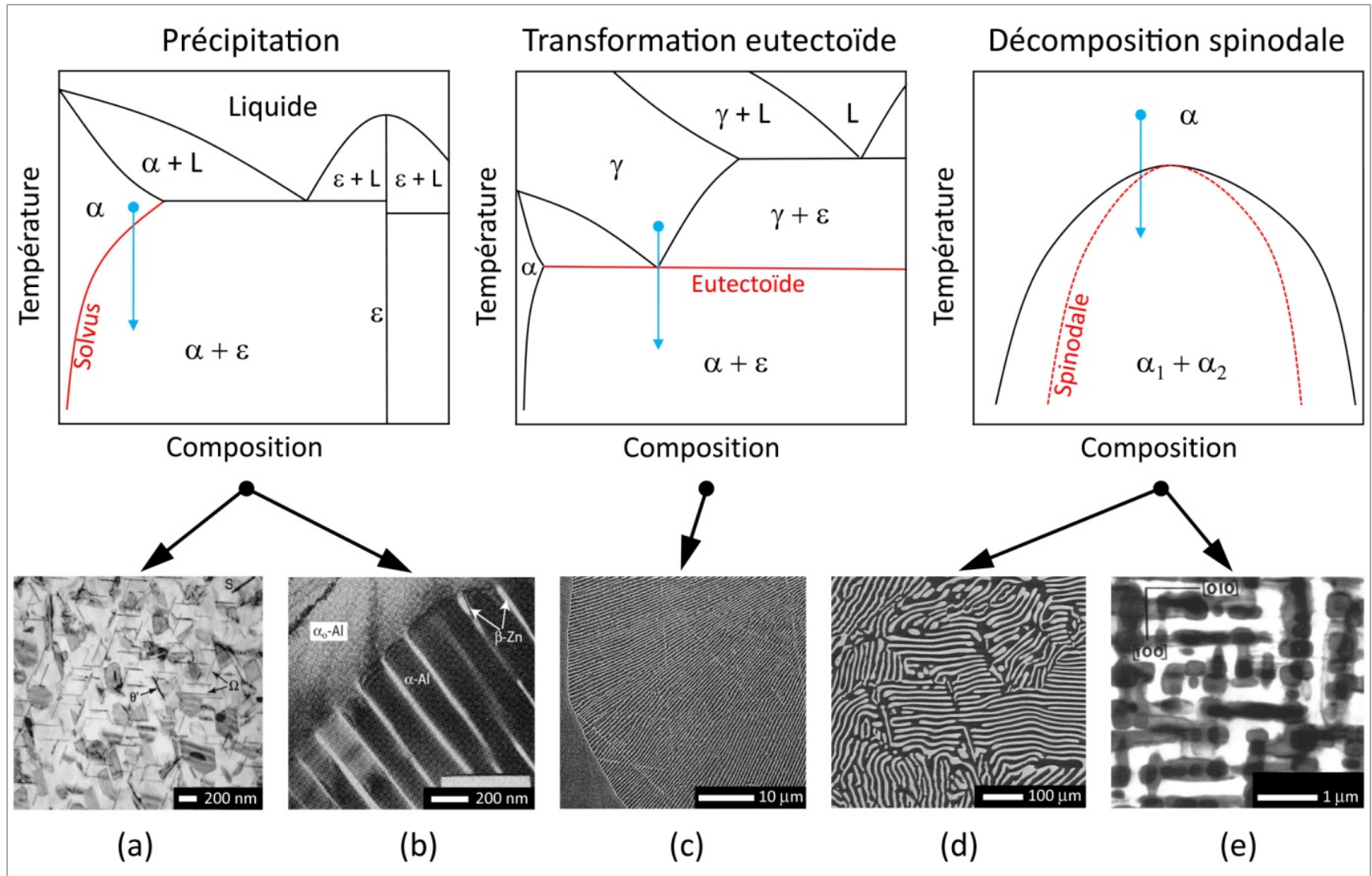
Interfaces, nano défauts

- diminution du libre parcours moyen des phonons

$$\kappa_{ph} = \frac{1}{3} C v \lambda_{ph}$$

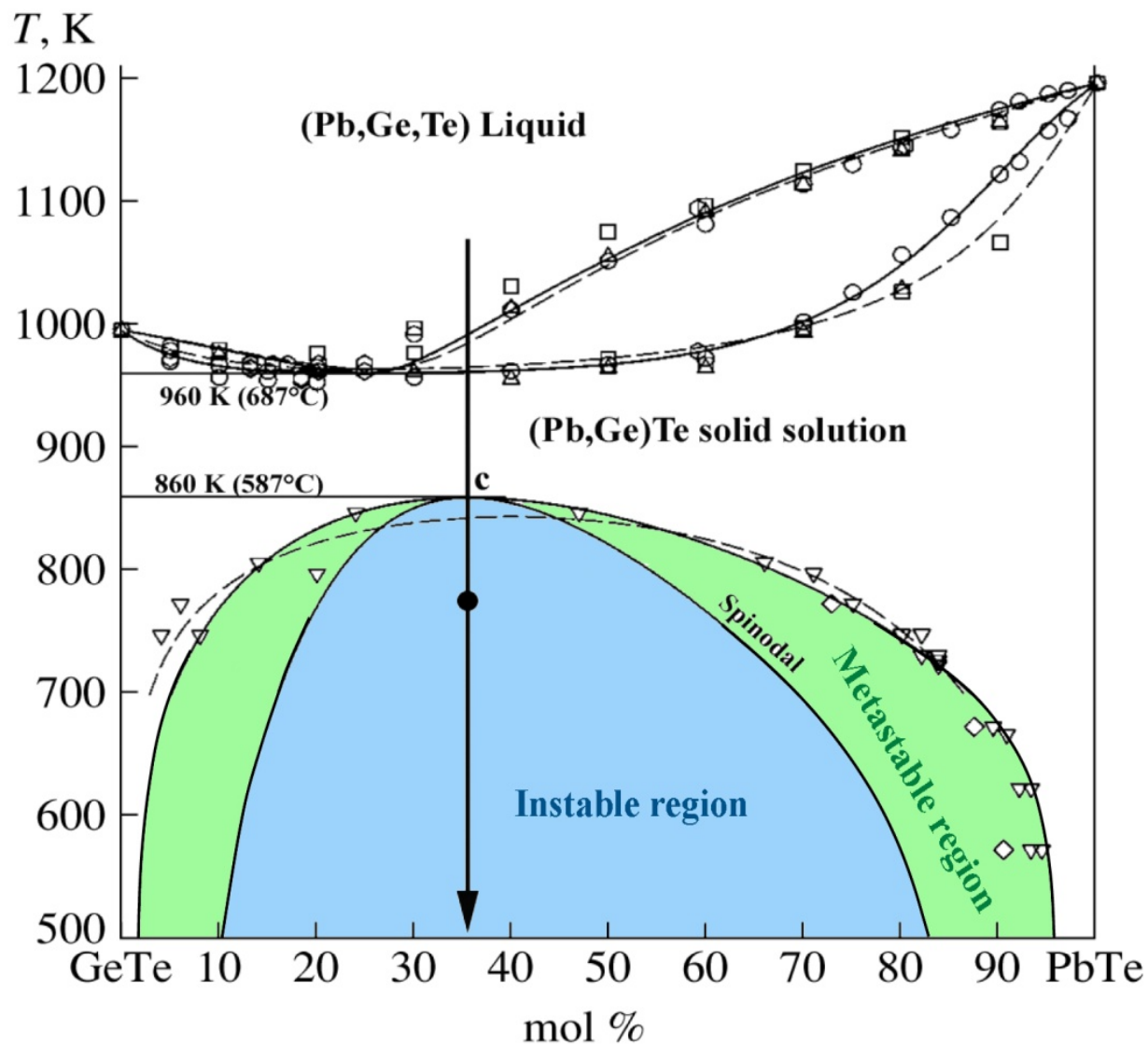
- abaisse la conductivité thermique de réseau sans affecter le transport électronique

Vers des matériaux sur mesure



Les matériaux thermoélectriques : de l'importance de la microstructure

Synthèse du motif lamellaire PbTe/GeTe



Les matériaux thermoélectriques : de l'importance de la microstructure

Modélisation - *Décomposition spinodale discontinue*

Transformation discontinue

$$v = -M_F \Delta G$$

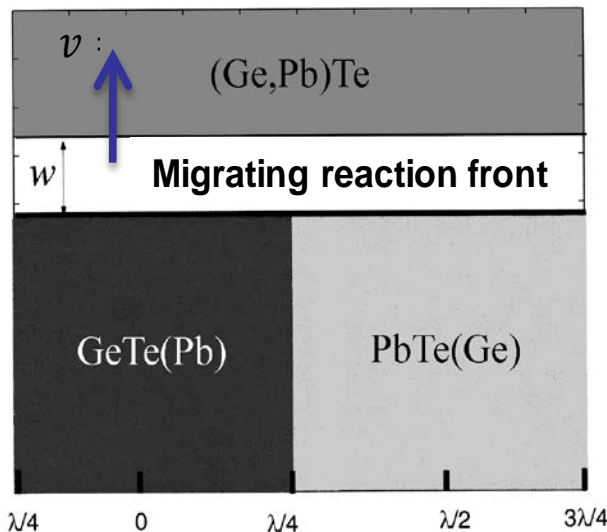
Cahn, Acta Metall. 7 (1959) 18.

Décomposition spinodale

$$\frac{\partial c(x,t)}{\partial t} = M \left[\frac{\partial^2 G}{\partial c^2} \nabla^2 c - 2\kappa \nabla^4 c \right]$$

Cahn, Acta Metall. 9 (1961) 795.

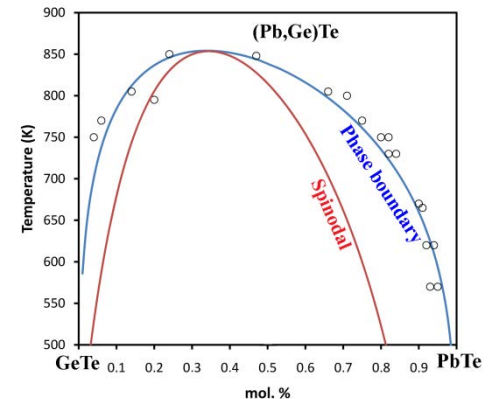
$$v = \frac{-M_F c_\beta^2}{8} \left(\frac{\partial^2 G(c_0)}{\partial c^2} \right)$$



- $M_F = \beta(D\delta/b^2 RT)$ Turnbull, Trans AIME 191 (1951) 661

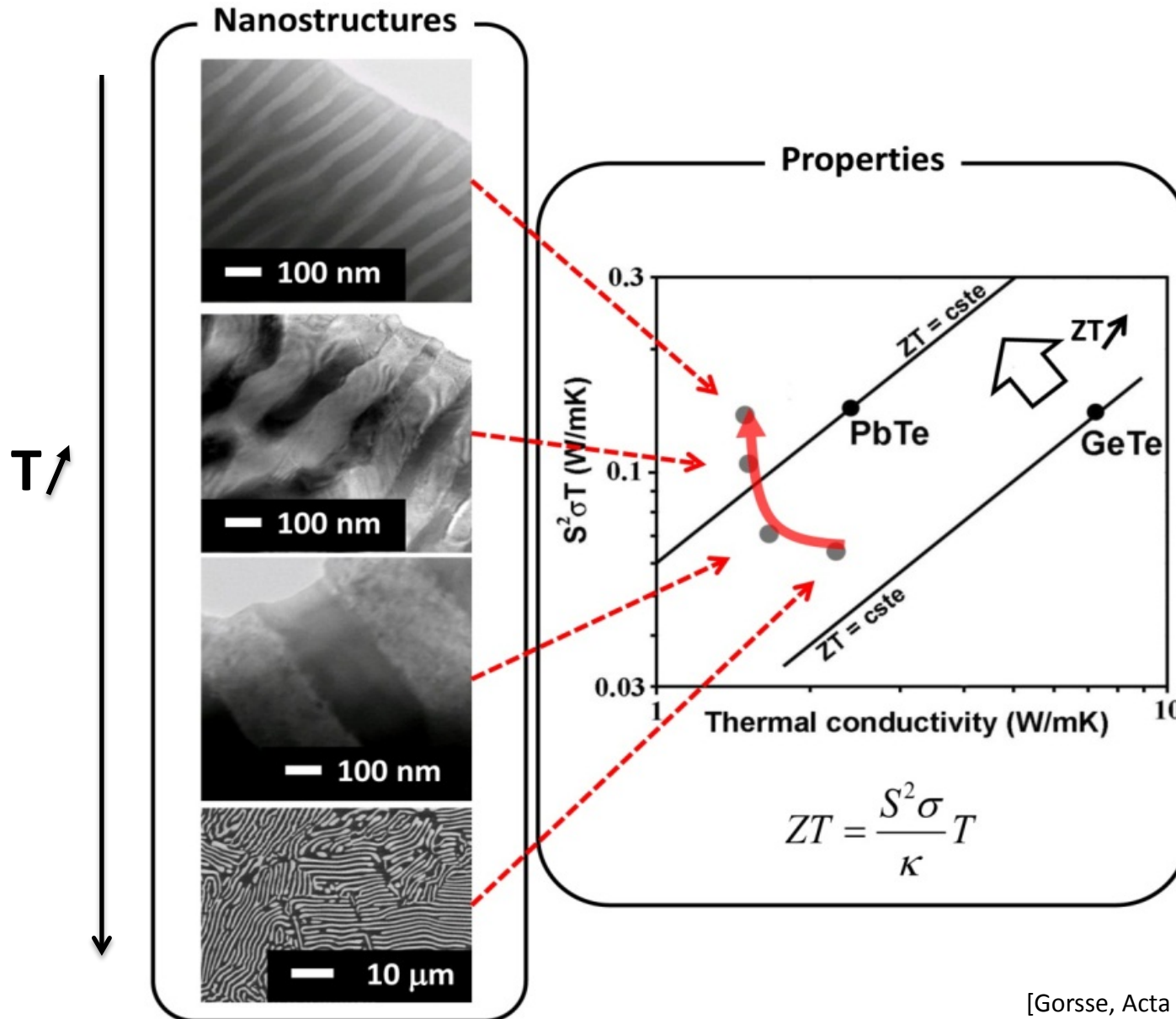
- $C_\beta \rightarrow$ Profils de concentration

- $\frac{\partial^2 G(c_0)}{\partial c^2}$



$$G = \sum c_i \mu_i - T[-R(c \ln c + (1-c) \ln(1-c))] + c(1-c)[{}^0L + {}^1L(1-2c)]$$

Vers des matériaux sur mesure



***Les conducteurs musclés: jouer
sur le procédé***

Matériaux pour les électro-aimants à haut champ

$$H_0 = j\lambda a_1 F(\alpha, \beta)$$

- Contenir le champs magnetic sans rompre
- Ne pas excéder un chauffage admissible

$$\sigma_y \geq \frac{H_0^2}{F(\alpha, \beta)}$$

$$H_0 \leq \left(\frac{\Delta T_{\max} \lambda c_p \rho}{t_p \rho_e} \right)^{1/2} a_1 F(\alpha, \beta).$$

Cartes de selection

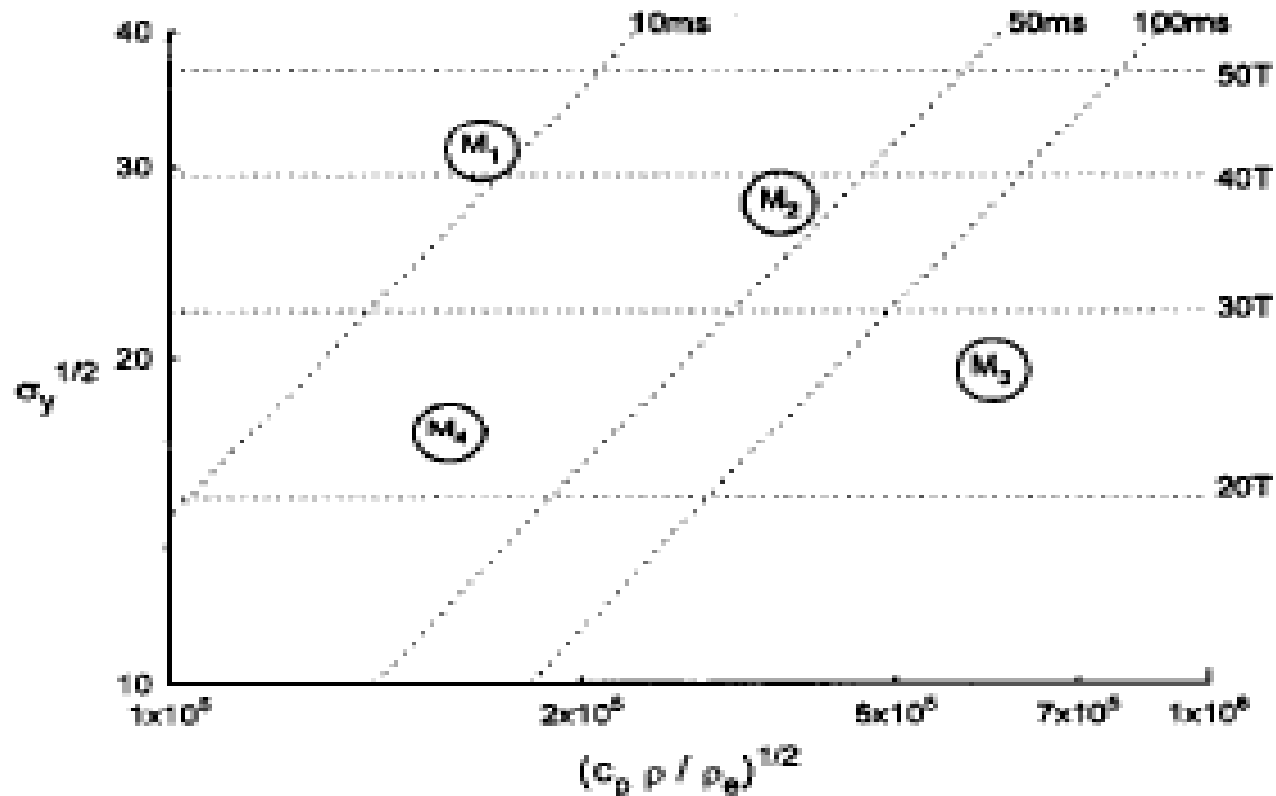


Fig. 2. Materials selection chart for high-field, pulsed magnet coils. Material M_1 is the best choice for short pulses of very high field, M_3 for long pulses at lower field, and M_2 for intermediate fields and pulse lengths. Material M_4 is less good than all the others under all conditions.

Candidats

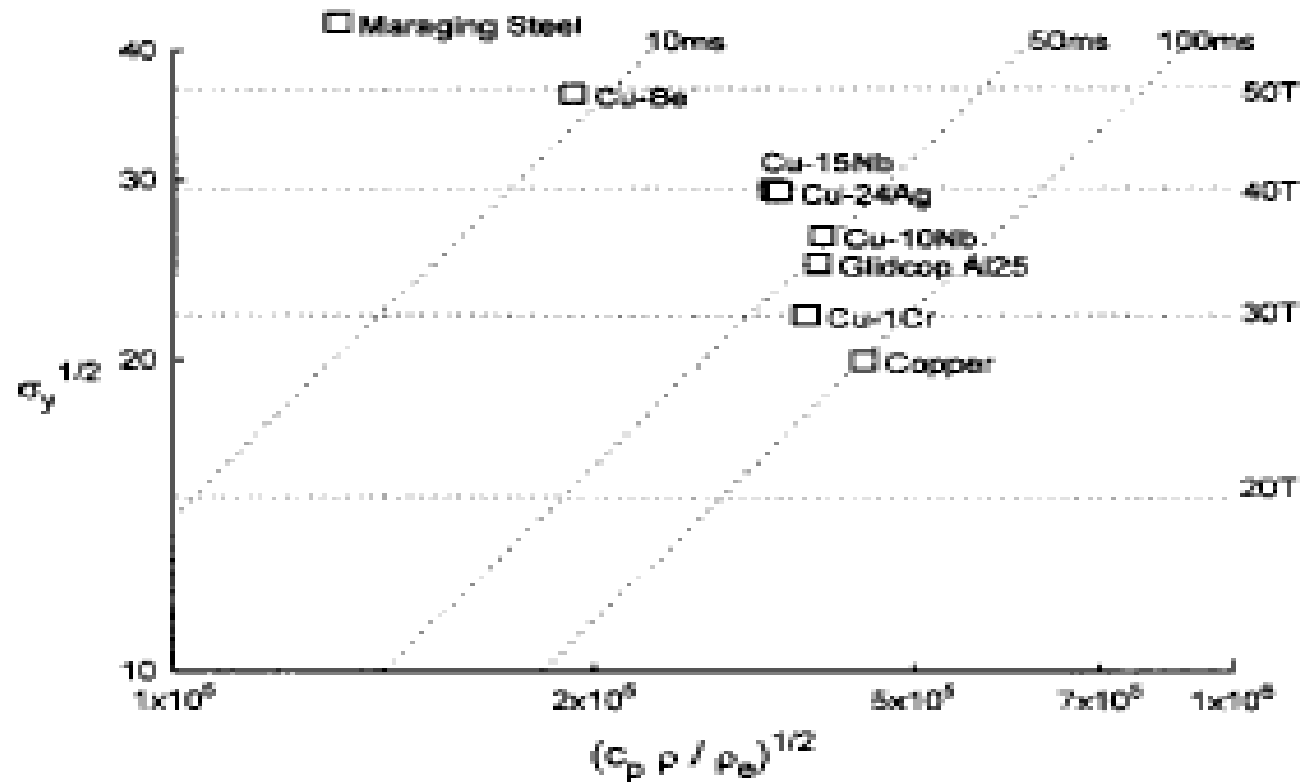
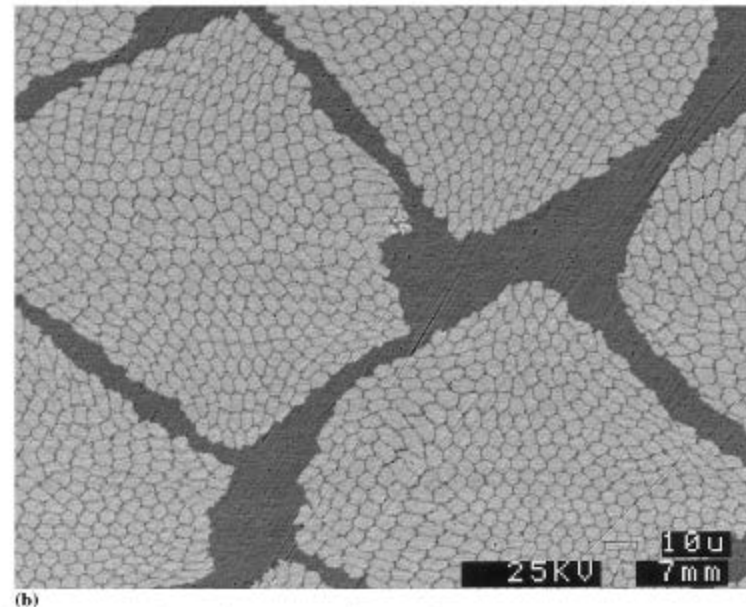
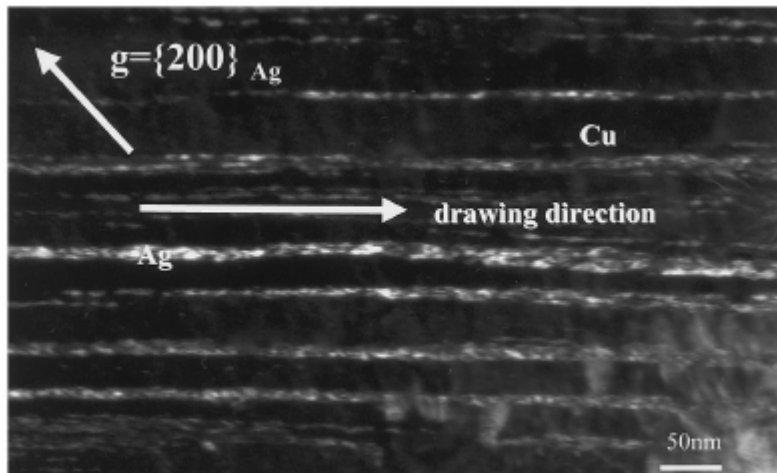
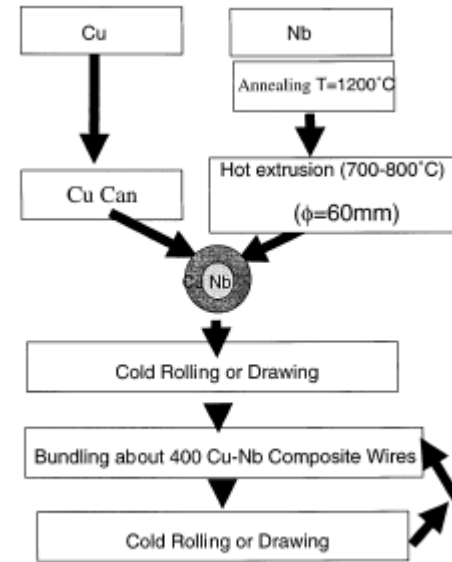
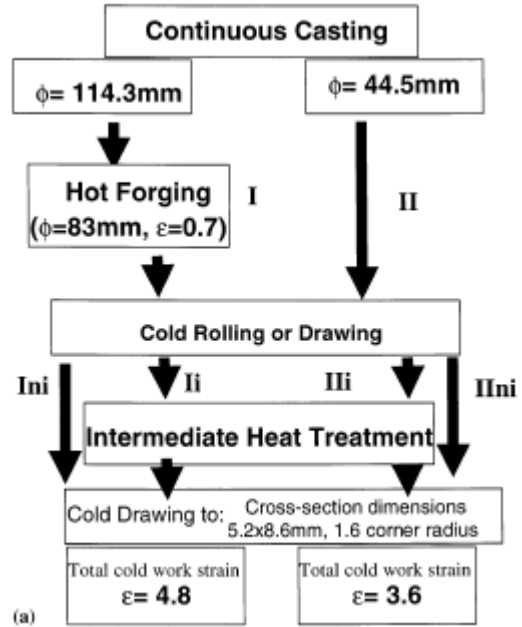


Fig. 3. Materials selection chart showing relative positions of various candidate materials.

Composites base cuivre



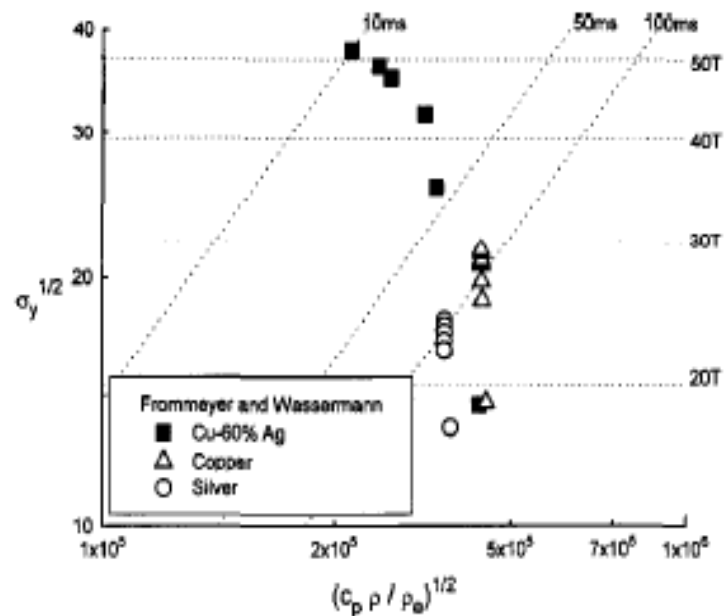


Fig. 4. Effects of cold work on properties of copper, silver and Cu 60 at.%Ag [4, 5].

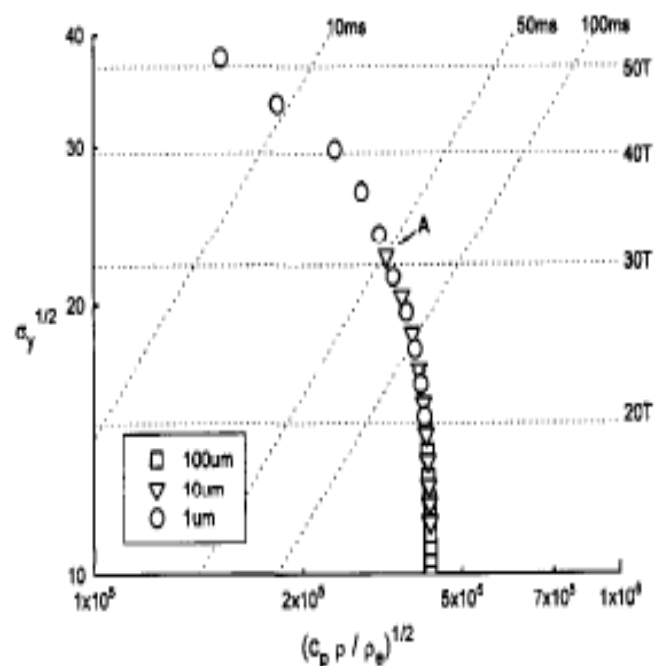


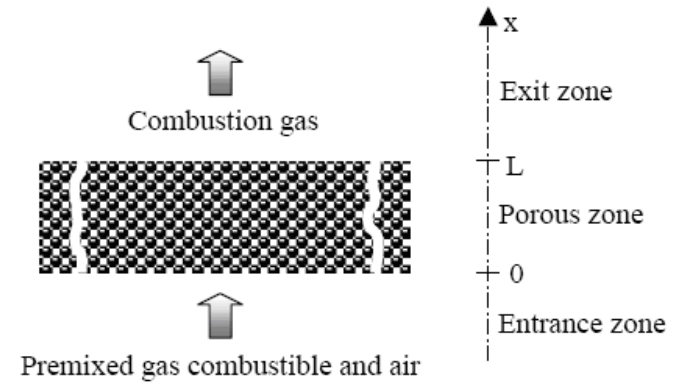
Fig. 5. Evolution of properties with cold work for various initial interphase spacings.

$$\sigma = \sigma_0 + \frac{k}{\sqrt{\lambda_0}} \exp(\epsilon/4)$$

$$\rho = \begin{cases} \rho_0 \left[1 + \frac{3\bar{x}}{4\lambda_0} \exp(\epsilon/2) \right] & \lambda \gg \bar{x} \\ \rho_0 \left[\frac{\bar{x}}{\lambda_0} \right] \exp(\epsilon/2) & \lambda \ll \bar{x} \end{cases}$$

L'architecture comme levier d'optimisation

Concevoir un brûleur radiant



| Constraints | Objectives | Free variables |
|--|--|---------------------------------|
| <p><i>Materials:</i> resisting at high temperature, in oxidative atmospheres, and to thermal choc.</p> | <p>High radiation emission</p> <p>Low pollutant emission</p> | <p>Architectural properties</p> |
| <p><i>Functioning:</i> the flame front inside the porous zone</p> | <p>Wide range of in-flux</p> | <p>Constitutive materials</p> |

Modelling tools

- **Combustion modelling**
 - Fluid transport, heat transport
 - Radiative transfer
 - Reaction rates $fct(T)$, chemical products
- **Materials modelling**
 - Permeability
 - Thermal properties (thermal capacity, conductivity, radiative power)

Preselection for the constitutive materials

| Base materials (purity ratio) (bulk density) | Current acronym | Cells/Volume (1/mm ³) | Relative density |
|---|--|--------------------------------------|---------------------|
| Alumina (99.8%) (1.2) | Alumina | 300-6 x10 ⁺⁴ | 0.297-0.328 |
| Alumina (99.8%) (0.8) | Alumina | 300-6 x10 ⁺⁴ | 0.198-0.219 |
| Alumina (99.8%) (0.4) | Alumina | 300-6 x10 ⁺⁴ | 0.099-0.109 |
| Alumina (99.5%) (0.745) | Alumina | 0.20-88 | 0.17-0.22 |
| Alumina (92%) (0.61) | Alumina | 0.28-110 | 0.13-0.18 |
| Alumina (99%) (0.825) | Alumina | 0.10-15 | 0.205-0.215 |
| Cordierite (0.5) | Cordierite | 0.10-15 | 0.16-0.18 |
| Mullite (0.70) | Mullite | 0.10-15 | 0.23-0.24 |
| Mullite (0.65) | Mullite | 0.10-15 | 0.215-0.225 |
| Mullite (NCL) (0.46) | Mullite-NCL | 0.20-42 | 0.15-0.16 |
| Silicon Carbide (0.5) | SiC | 0.10-15 | 0.15-0.16 |
| Zirconia (Partly Stabilized) (1.28) | PSZ | 0.10-15 | 0.205-0.215 |
| Zirconia (Partly Stabilized) (1.27) | PSZ | 0.10-15 | 0.21-0.22 |
| Zirconia (Partly Stabilized) (1.23) | PSZ | 0.10-15 | 0.195-0.205 |
| Zirconia Mullite Alumina (0.63) | ZrO ₂ -Al ₂ O ₃ - | 0.33-57 | 0.15-0.19 |
| | SiO ₂ | | |
| Zirconia with Calcia (Fully Stabilised)(0.74) | ZrO ₂ -CaO | 2.30-38 | 2.24 |
| Zirconia with Magnesia (Partly Stabilised)(0.81) | ZrO ₂ -MgO | 0.50-60 | 0.123-0.147 |

Pre-Selection

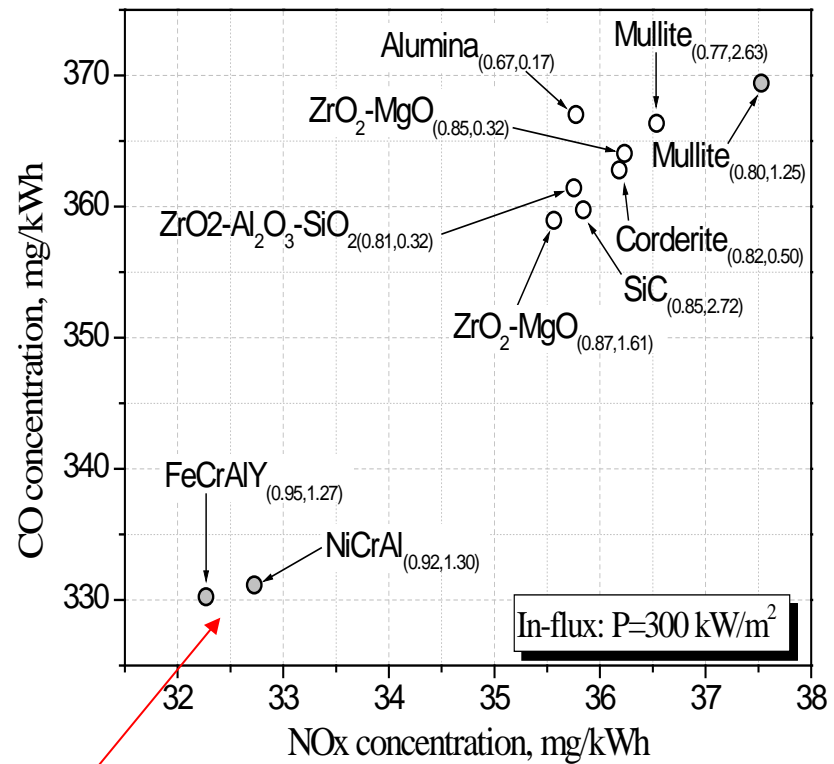
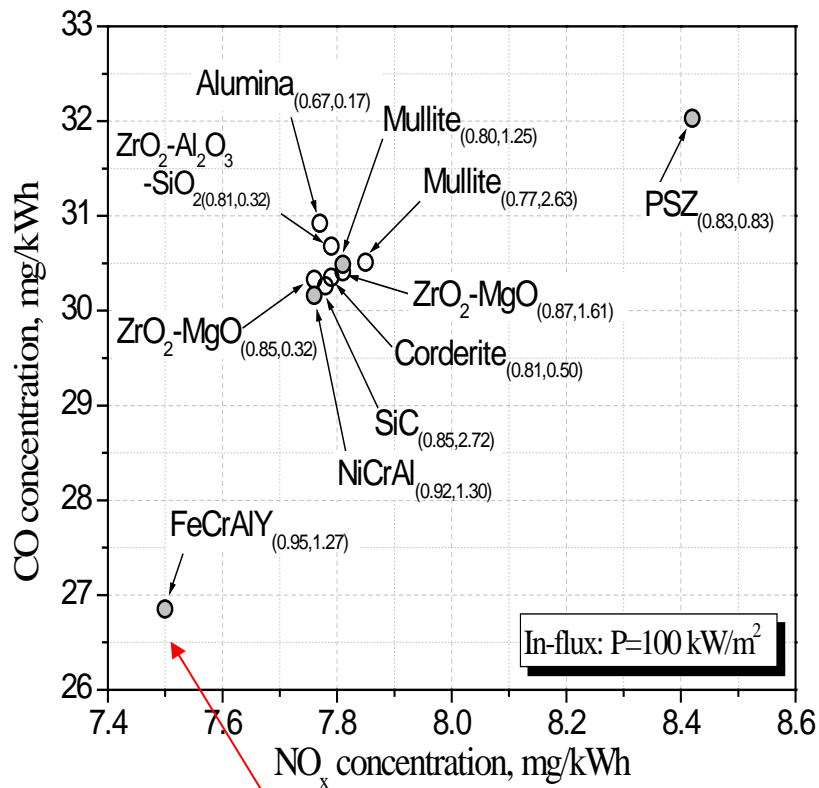
On the operating
Temperature,

On the oxydising
Atmosphere

On the ability to make
a foam, A felt...

| Additional materials | Porosity | Cell size-Strut size, mm | Specific area, mm ⁻¹ |
|----------------------|----------|-----------------------------|------------------------------------|
| FeCrAlY | 0.951 | 1.27-0.23 | 2.00 |
| NiCrAl | 0.928 | 1.30-0.26 | 2.45 |
| Mullite | 0.809 | 1.25-0.19 | 3.60 |
| PSZ | 0.832 | 0.83-0.19 | 4.43 |

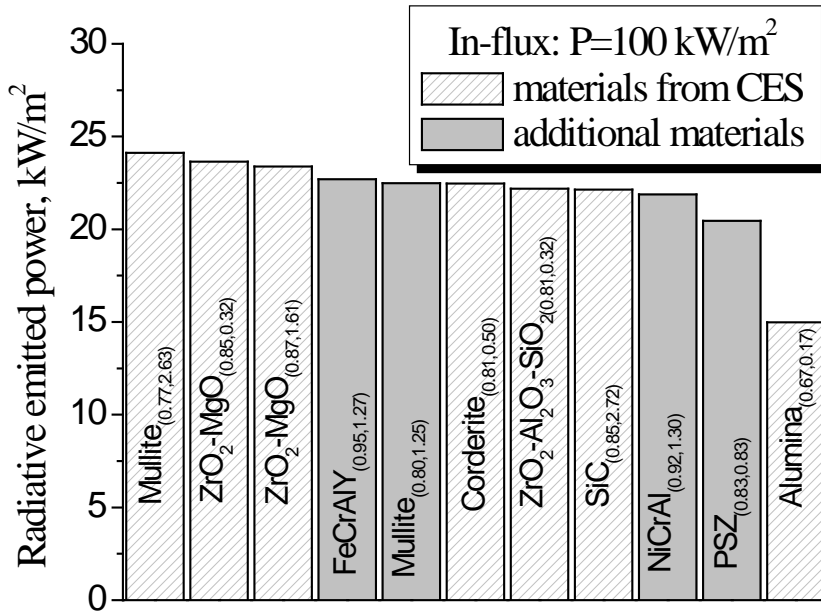
CO₂/NO_x emission



Less pollution
FeCrAlY, NiCrAlY

Cell size 1.2mm, porosity 90%

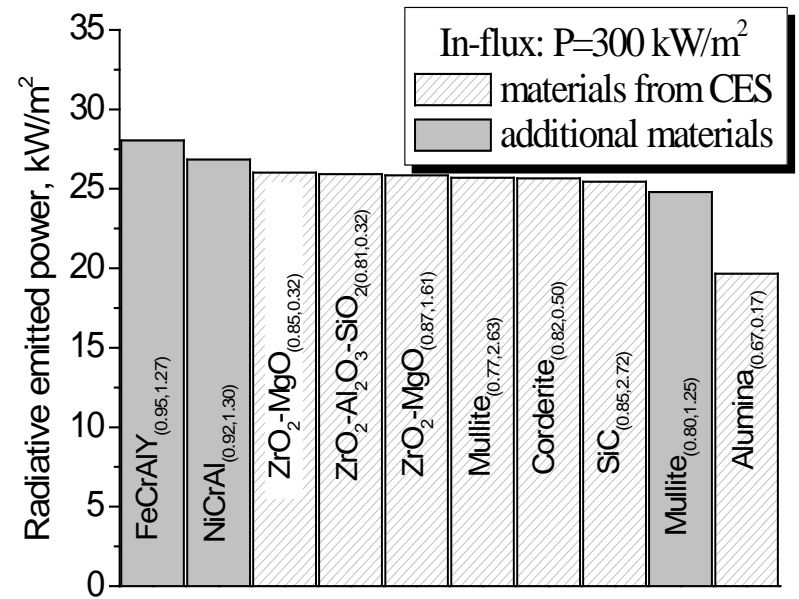
Radiative power



Material constituting the burner

Best energy efficiency
Mullite

Cell size 1.2mm,
porosity 90%

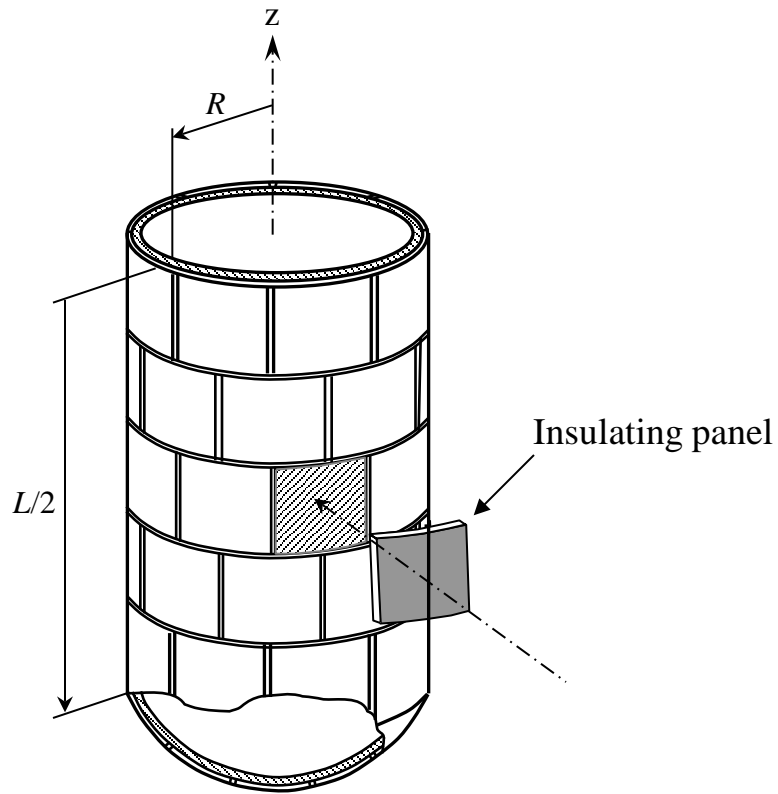


Material constituting the burner

Best energy efficiency
FeCrAlY

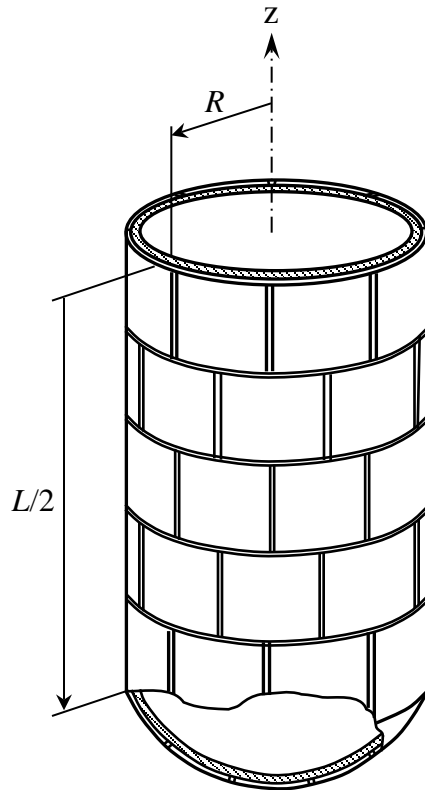
Isolants ablatifs

- ▶ For large cryogenic reservoirs \Rightarrow disconnected glued panels as the *TPS*

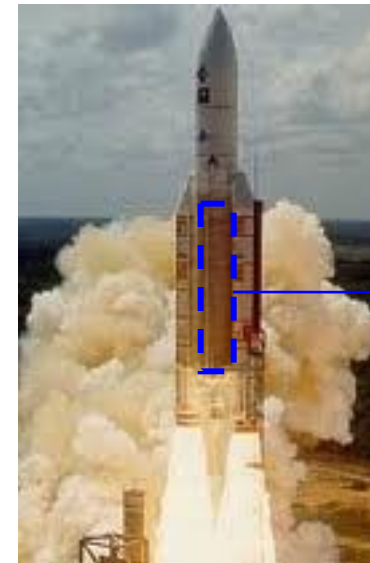


Half part of large cryogenic reservoir

- ▶ For large cryogenic reservoirs \Rightarrow disconnected glued panels as the *TPS*



Half part of large cryogenic reservoir

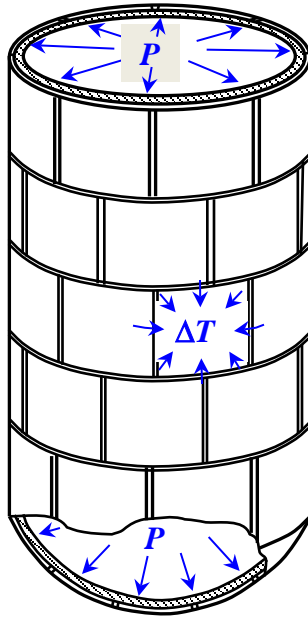


| |
|--------------|
| Height |
| $L = 23$ m |
| Diameter |
| $2R = 5.4$ m |

e.g. Cryogenic Main Stage (EPC) of Ariane 5

After the fuelling, the structure is subjected to:

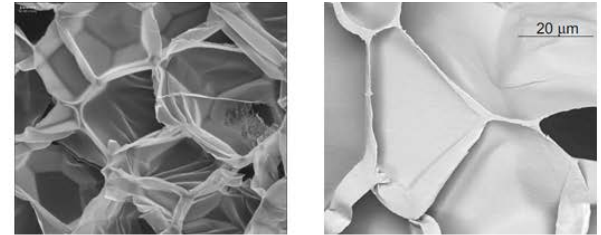
- the fuel pressure, $P \approx 3$ Bars
- and a cooling of $\Delta T \approx -270$ K, leading to thermal stresses



The insulation should be also dimensioned to withstand the combined pressure and thermal loads !!!

Half part of large cryogenic reservoir

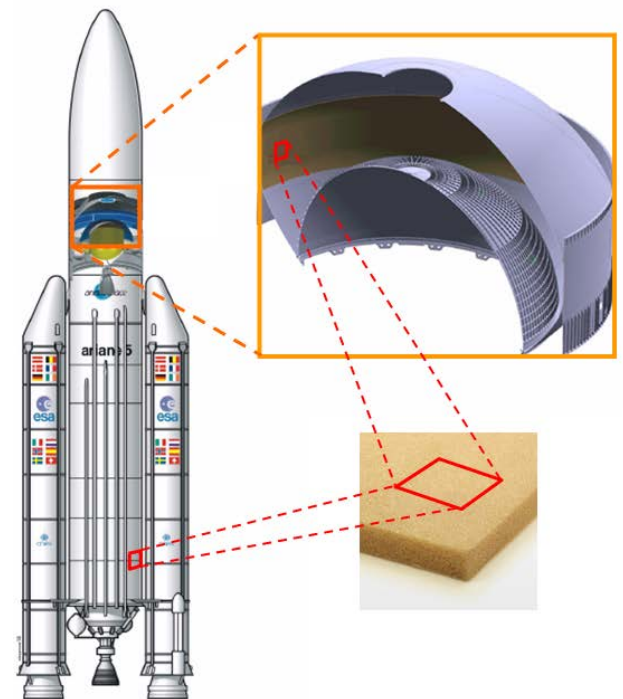
- Polymer foams are attractive engineering materials for light weight structural insulation application.
- Thermal insulation of rocket cryogenic tanks is an example where the foam panels are glued on the metallic shells.
- The requirements imposed on the insulation system are:
 - light-weight;
 - strength to withstand thermal stresses and structure loads;
 - resistant to aero-thermal ablation;
 - thermally resistant to minimize fuel boil-off.



Typical SEM photographs of XPS foam

Objective

- Predict the LH2 boil-off during ground and ascent phases and the insulation degradation resulting from the polymer foam ablation by the aero-thermal flux in flight.
- Identify insulation features enabling us to better meet the design requirements.



Hypothesis

- The fluid/wall heat exchanges modeled through convection coefficients.
- Foam ablation takes place above degradation temperature due to shear force of air flow.
- Ablation processes modeled as phase change phenomenon with propagation front tracking.

Governing equations

Energy equation:

$$\rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[k \frac{\partial T}{\partial x} \right]$$

Model of foam properties with thermal degradation:

$$C = \begin{cases} C_{foam} & \text{for } T < T_d - \Delta T_d / 2 \\ L_d / \Delta T_d & \text{for } T_d - \Delta T_d / 2 \leq T < T_d + \Delta T_d / 2 \\ 0 & \text{for } T \geq T_d + \Delta T_d / 2 \end{cases}$$

$$k = \begin{cases} k_{foam} & \text{for } T < T_d \\ \infty & \text{for } T \geq T_d \end{cases}$$

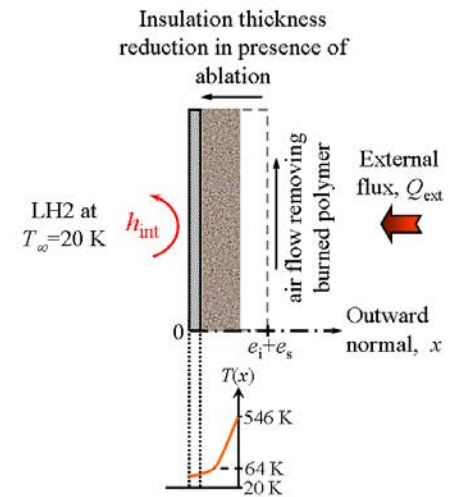
Boundary conditions:

$$h_{int} (T - T_\infty) = -k \frac{\partial T}{\partial x} \quad \text{at } x = 0$$

$$Q_{ext} = -k \frac{\partial T}{\partial x} \quad \text{at } x = e_i + e_s$$

At ground $t \leq 5$ min In flight $5 \text{ min} < t \leq 15$ min

$$Q_{ext} = h_{ext} (T - T_{ext}) \quad Q_{ext} = 3.5 \text{ kW} / \text{m}^2$$

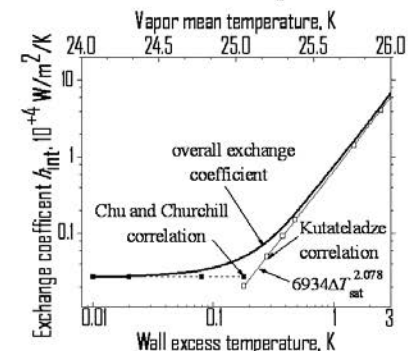
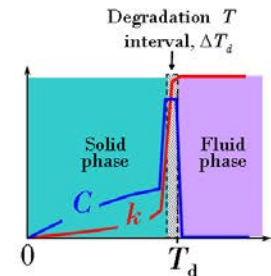


Insulation thickness reduction in presence of ablation

Illustration of the problem and typical temperature profile

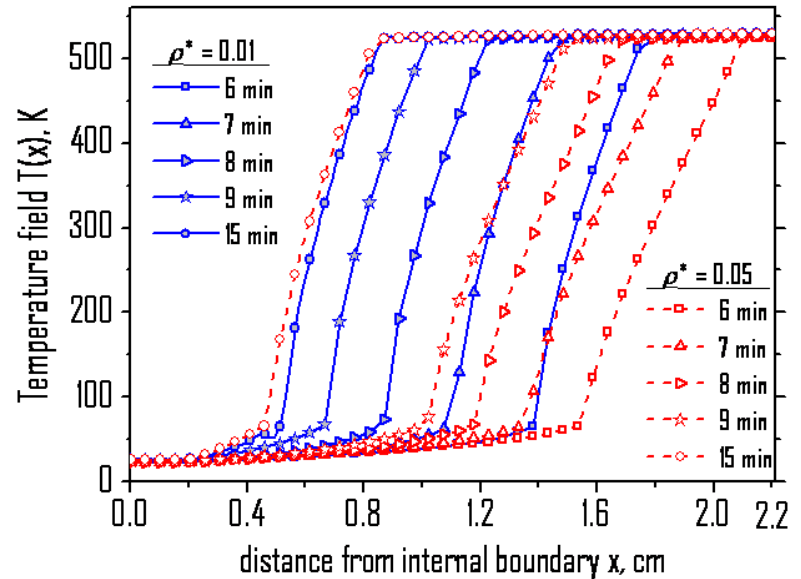
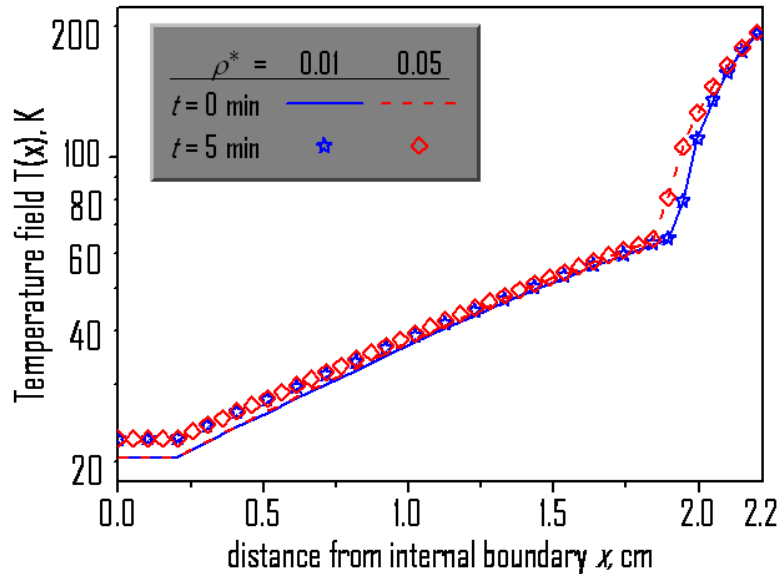
Typical wall parameters:

$$e_i = 20 \text{ mm} \text{ and } e_s = 2 \text{ mm}$$



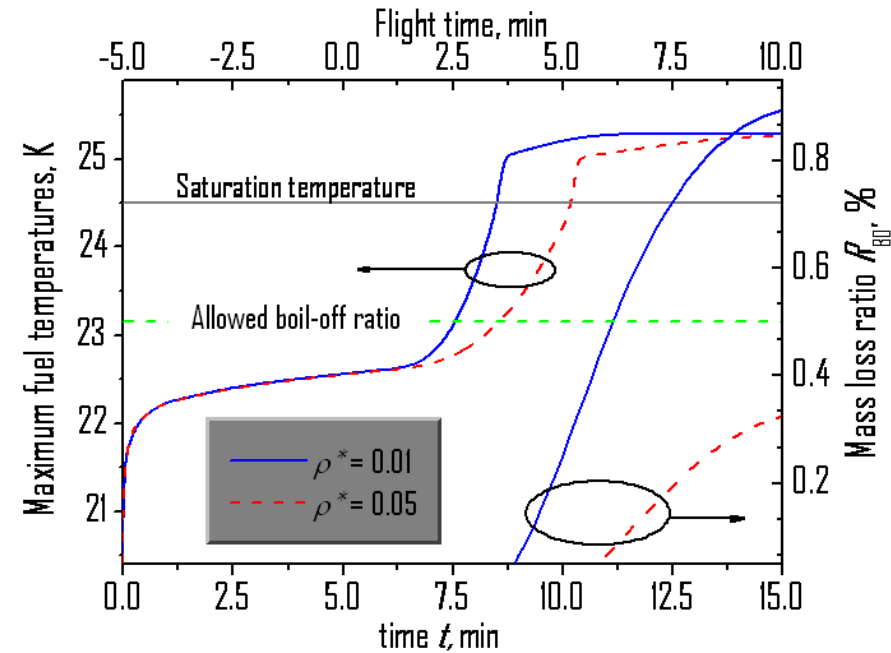
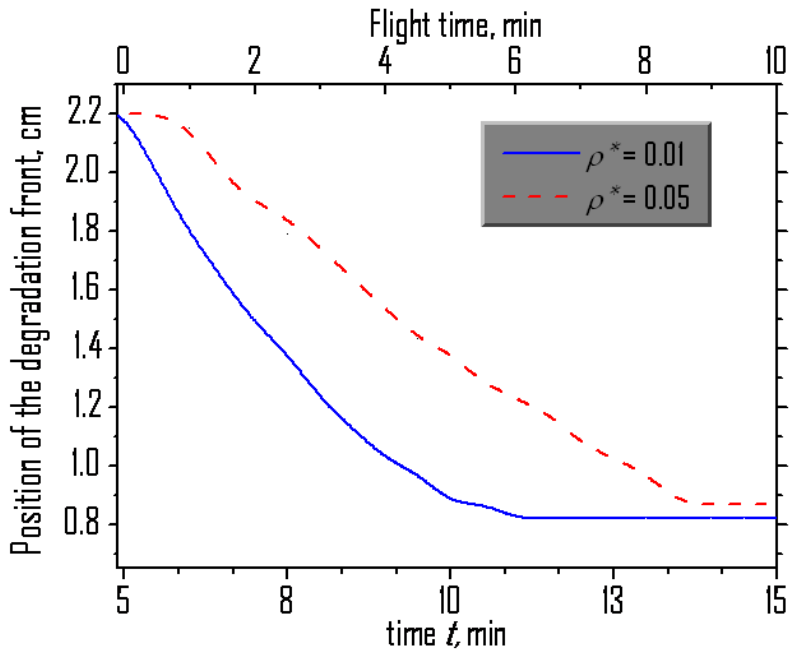
LH2-internal wall exchange coefficient

Temperature profile within walls. Insulation of uniform density



- During the ground phase (left figure), only the regions close to the internal boundary ($x = 0$) are warmed.
- In flight (right figure), the regions with quasi-constant temperatures above 500 K at time t mimics the ablated part of the insulation.
- The evolution of degradation front with time is given by the instantaneous positions of inflection points at 523 K.

Insulation ablation velocity, fuel temperature, boil-off



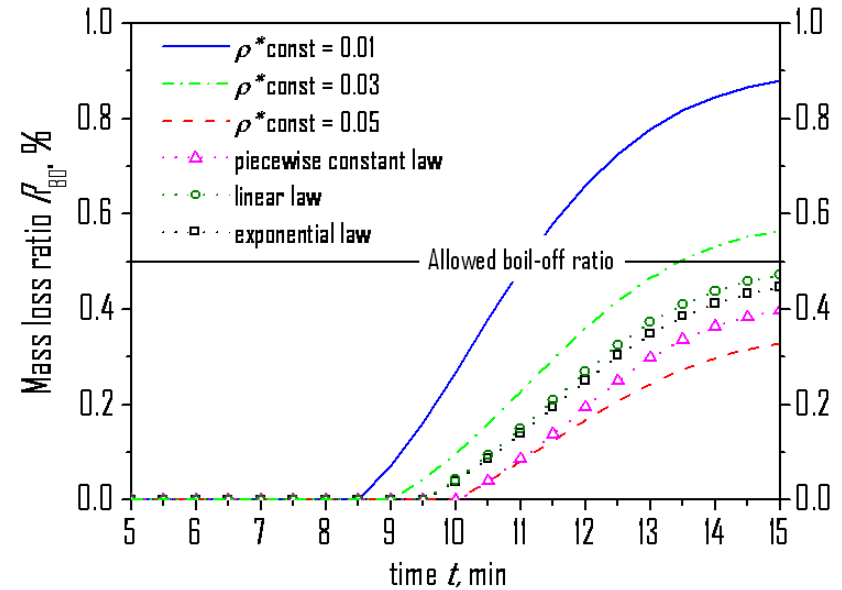
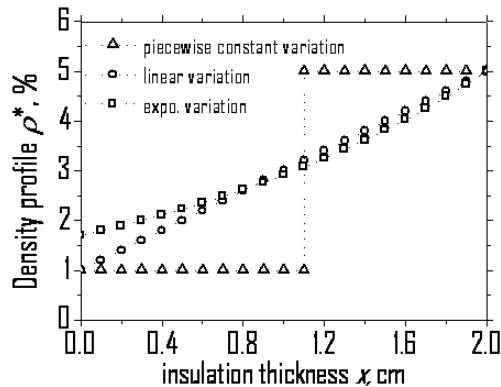
- The degradation starts some time after flight ($t > 5$ min) . It stops when the insulation becomes inefficient causing a total penetration of external flux.
- The lower the density, the faster the degradation is.
- The fuel temperature increases with time especially just after launch during which the incoming heat is removed slowly by the natural fuel flow.
- Then, nucleate fuel boiling removes heat rapidly and as result the maximum temperature increases moderately but in disfavor of the fuel boil-off.

Evolution of boil-off ratio for different insulation density profiles

Boil-off ratio, R_{BO} :

$$R_{BO} = \frac{\int_0^t \dot{m} dt'}{M} \quad \text{with} \quad \dot{m} L_{vap} = S h_{int} (T|_{x=0} - T_{sat})$$

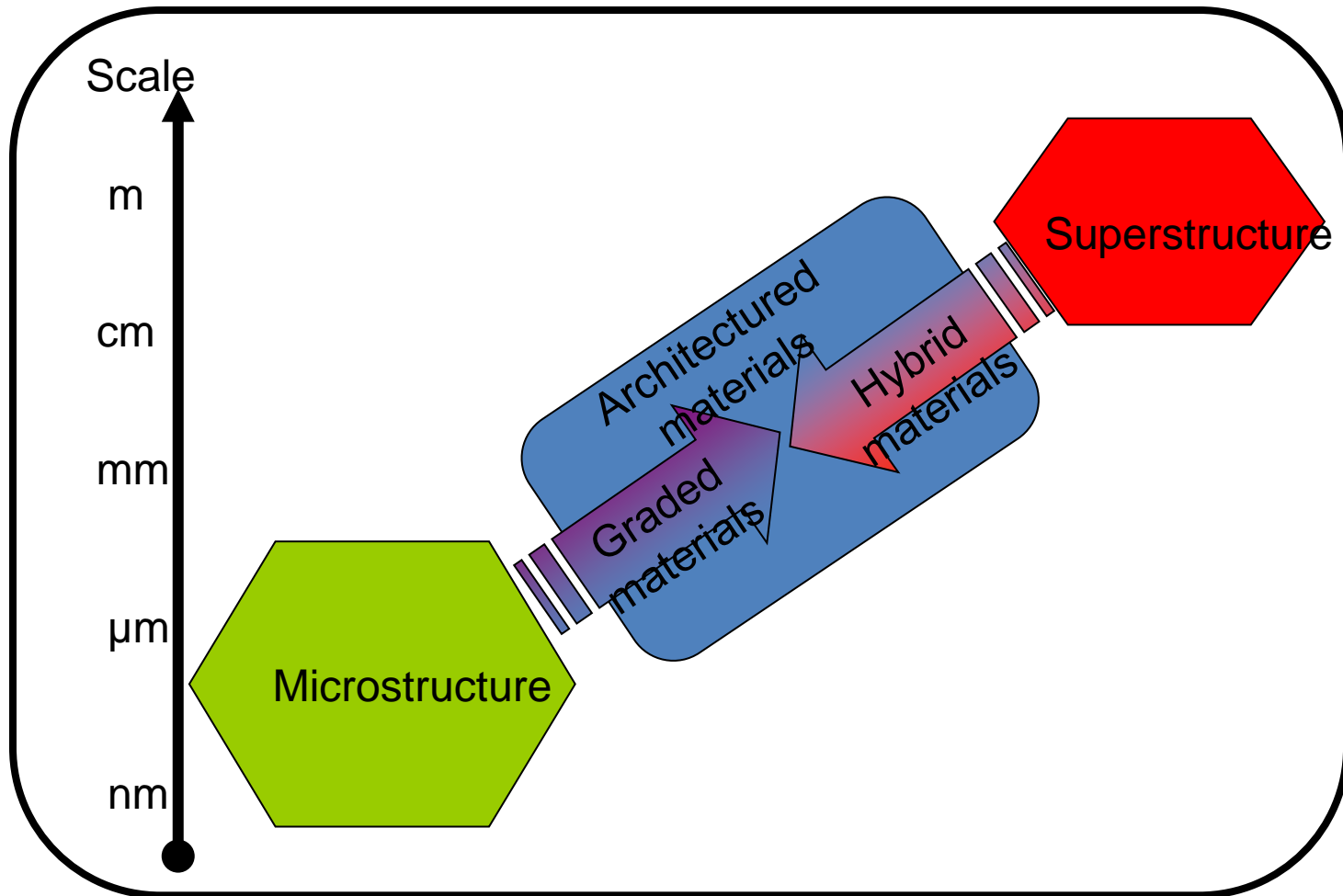
Density profiles of average density 0.03

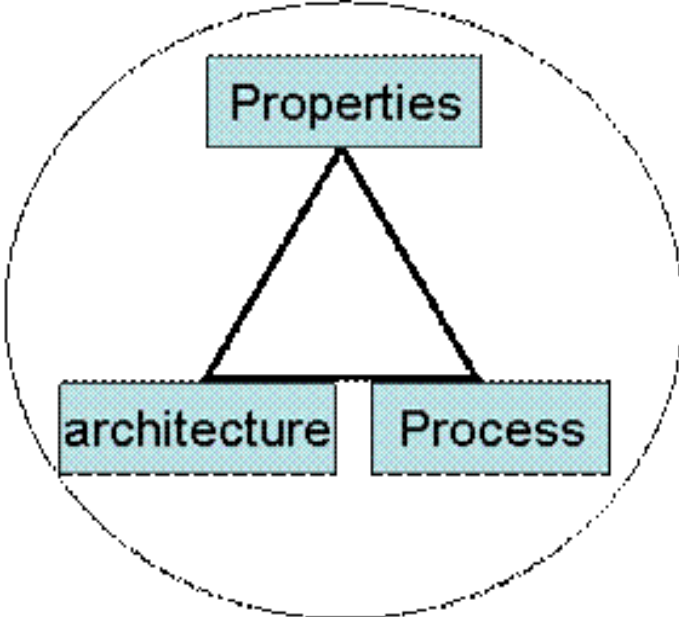


- The lower the density, the higher the boil-off ratio → there is a minimum density below which the boil-off exceeds the allowed value of 0.5 % of initial mass M .
- Insulation having graded density is more efficient than insulation of uniform density.
- Among the three graded density profiles, piecewise law provides the lowest boil-off ratio over the flight duration.

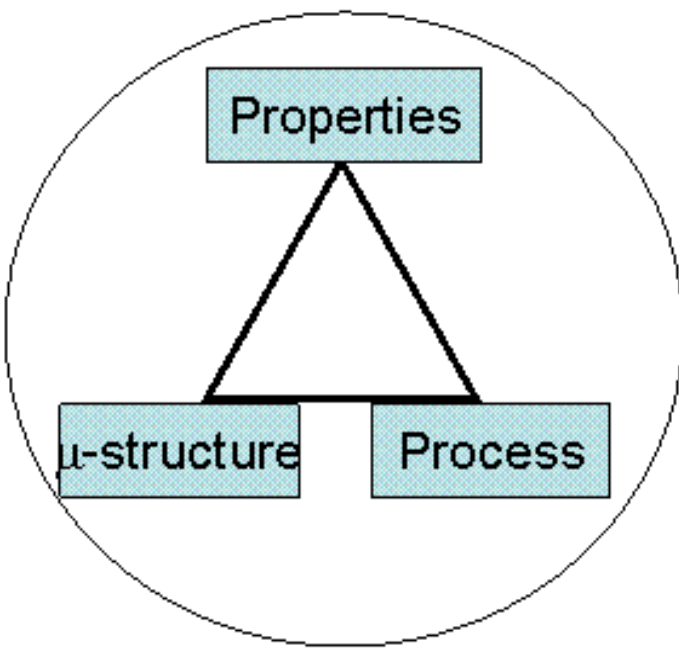
Conclusions

La stratégie multiéchelles





Microstructure + Architecture



Select Materials and Processes

Define Multifunctional Requirements