Low-temperature thick-film materials systems for electronic and sensor applications

Thomas Maeder	EPFL-Lausanne & Sensile Technologies
Claudio Grimaldi	EPFL-Lausanne
Sonia Vionnet-Menot	EPFL-Lausanne
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Hansu Birol	EPFL-Lausanne
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Huba Control

SENSILE TECHNOLOGIES

TOP NANO 21

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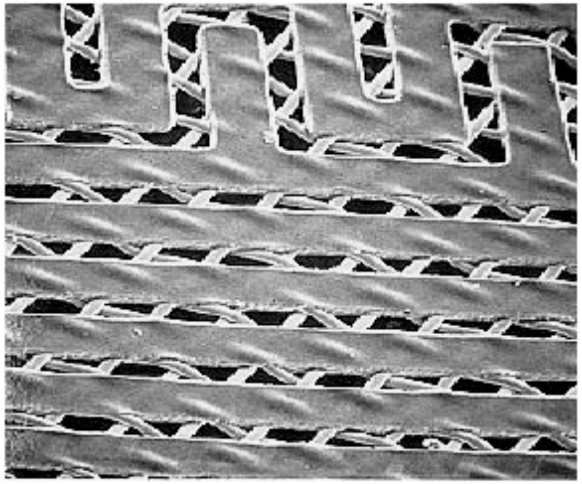
Summary

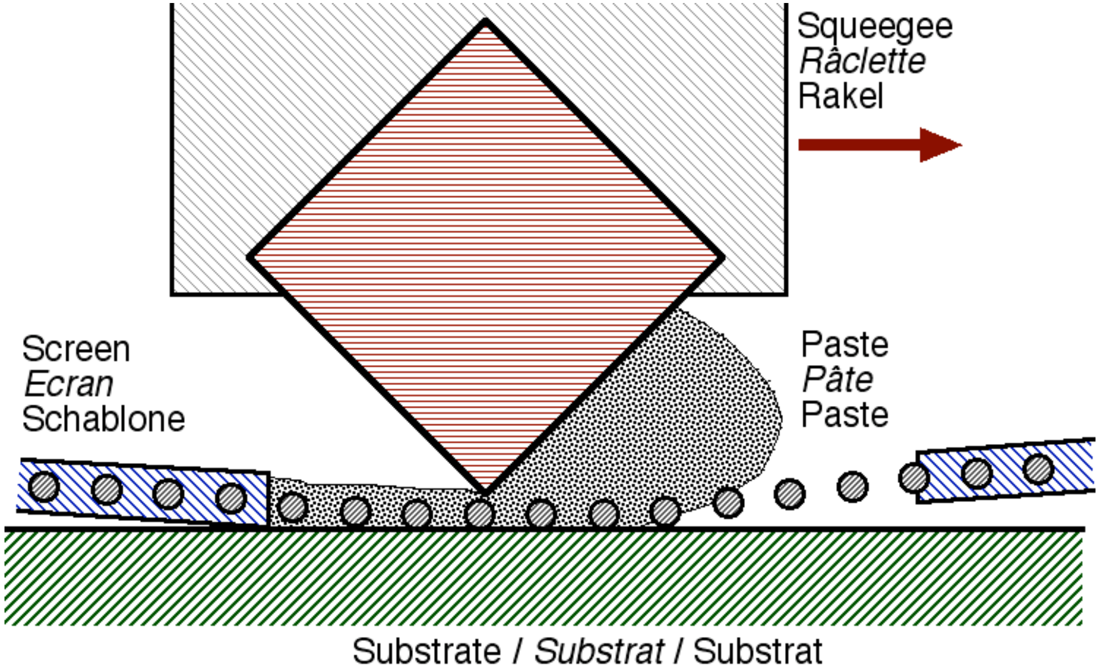
- Thick-film technology
- Thick-film (piezo)resistors
- Benefits of systems with a low firing temperature
- The (piezo)transport properties of low-temperature thick-film resistors
- Stabilisation of low-temperature dielectrics
- Demonstrators
- Conclusions & outlook

Overview of thick-film technology 1/3

Paste

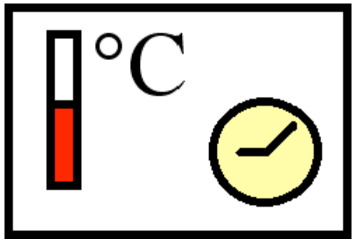


Screen

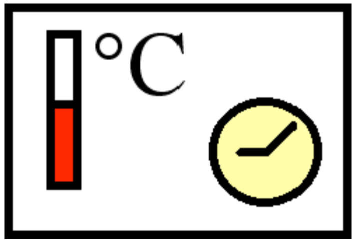


Screen printing

Overview of thick-film technology 2/3



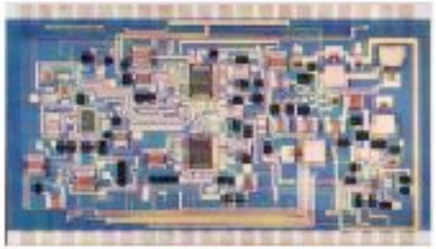
Drying
(typ. 150°C 10')



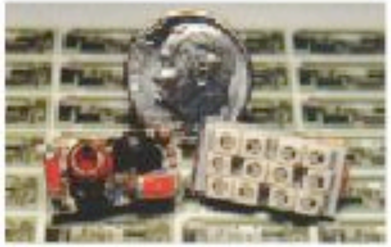
Firing
(typ. 850°C 10')

Laser
trimming

Overview of thick-film technology 3/3

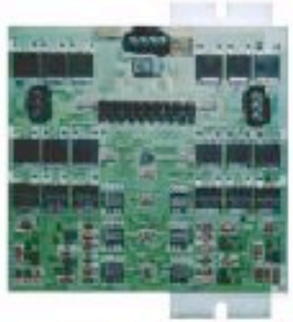


Médical
Multichip module (23 couches)

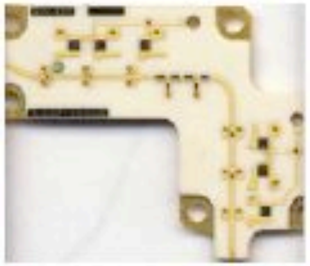


Aviation
Led pour Cockpit

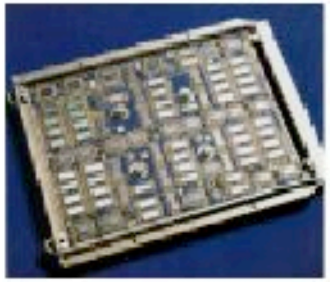
Instrumentation
Sonde active



Grand public
Périphérique d'ordinateur

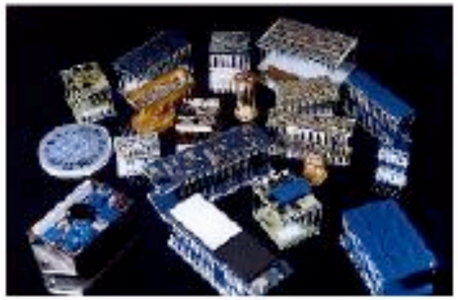


Radar
Module hyper fréquence



Militaire
Module mémoire

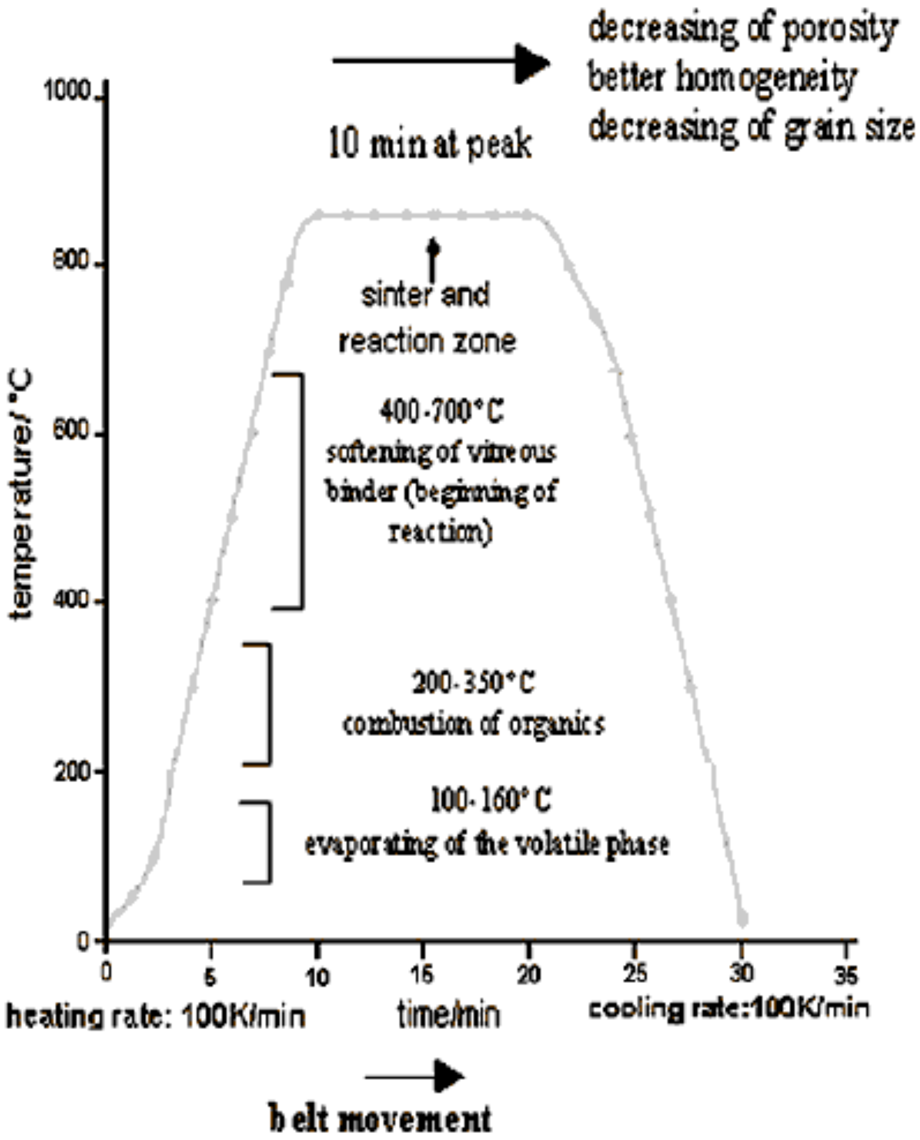
Automobile
Contrôleur de puissance



Exemple de packaging

Thick-film circuits

Thick-film firing process



- Debinding (burn-out of organics)
- Sintering
- Further reactions (crystallisation, etc.)

Thick-film materials types

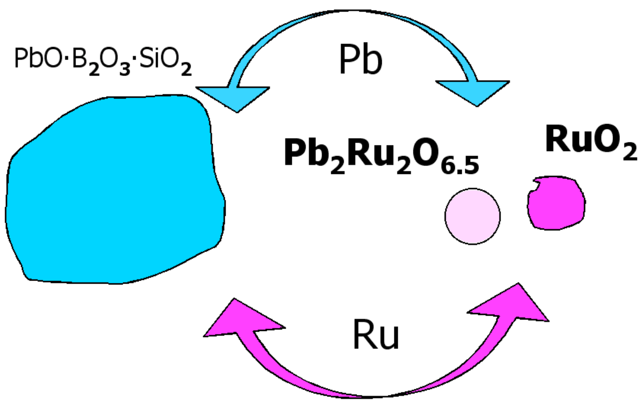
- Conductors
- Resistors
- Dielectrics
- Protective layers: glasses & polymers

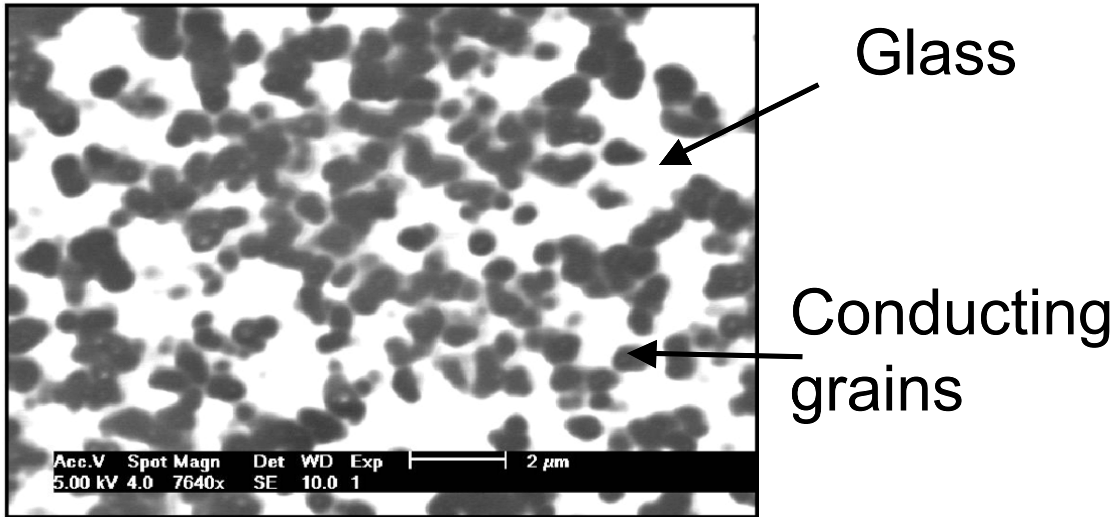
- Glues & sealing glasses
- Gas-sensitive ceramics: SnO_2,ZnO, Fe_2O_3,…
- Chemical electrodes: Pt, Au, RuO_2, …
- SOFC electrodes: Ni, (La,Sr,…)(Mn, Cr, Fe)$O_{3-\delta}$
- Piezo / pyroelectric ceramics: PZT,PMN, KNN,…

- Phosphors: sulfides, …
- Electron sources: MgO, …
- Field emitters: nanotubes, carbides, borides, …

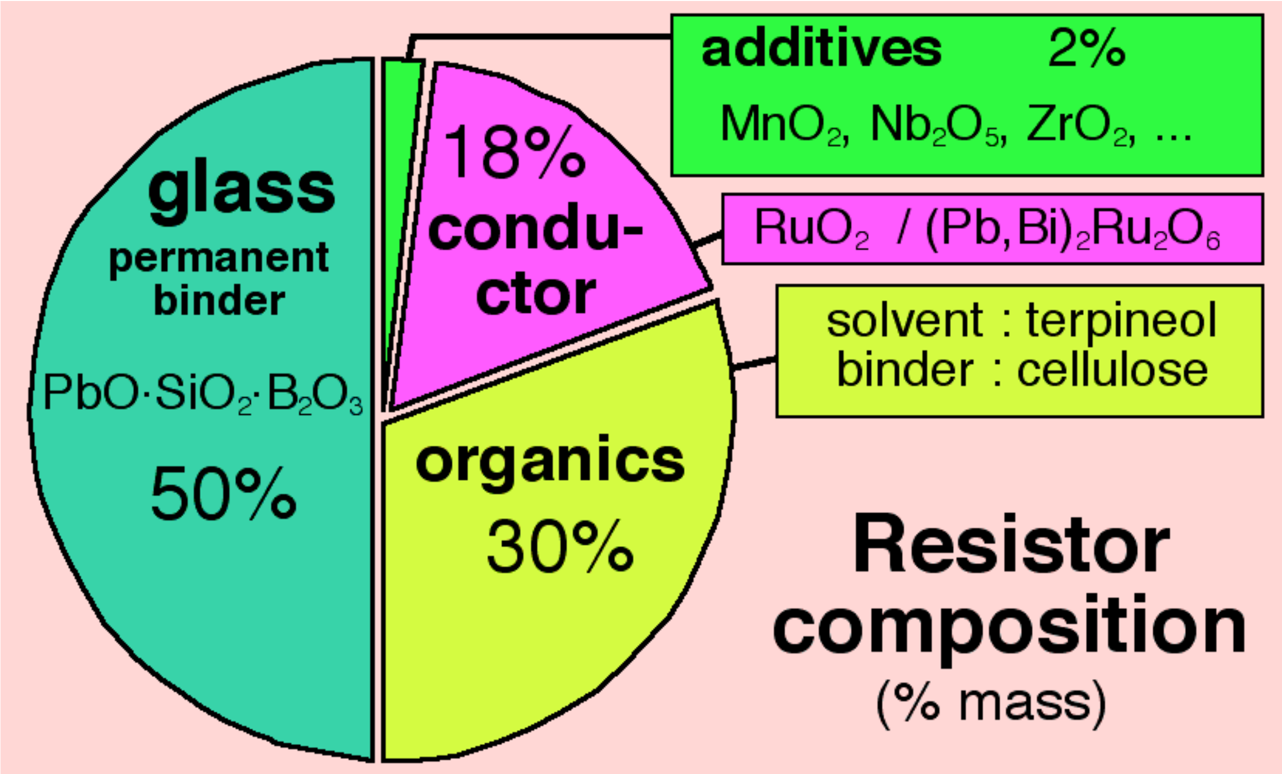
Thick-film resistors 1/4 - introduction

- Random dispersions of conducting nanoparticles in insulating matrix
- Insulating phase: typ. $PbO \cdot SiO_2 \cdot B_2O_3$ glass
- Conducting phase: typ. RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$
- Densification by liquid-phase sintering
- Further particle-glass interactions

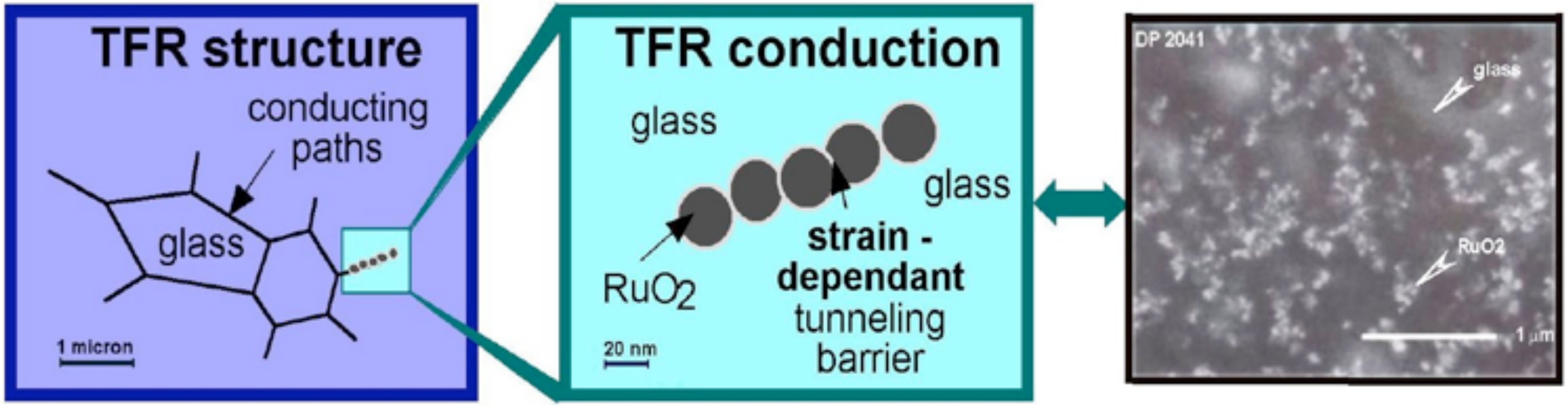




Thick film resistors 2/4 - composition & microstructure



Microstructure

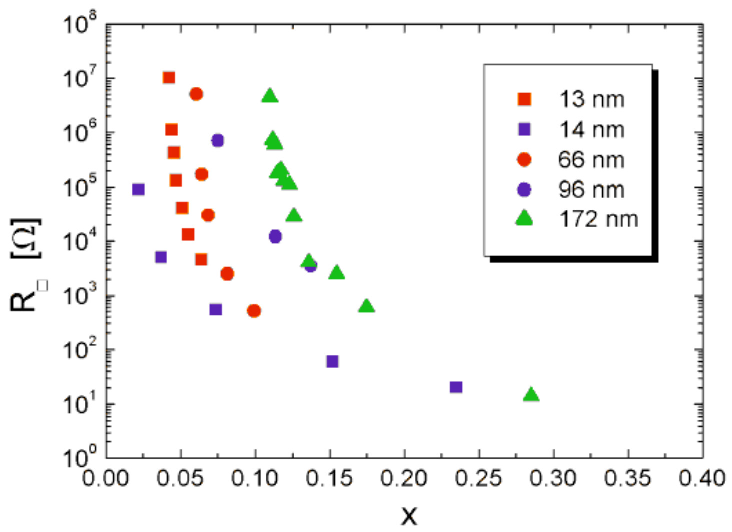


Thick-film resistors 3/4 - electrical transport

V_M = total volume of conducting particles

V_G = total volume of insulating grains

$$x = \frac{V_M}{V_M+V_G} \longrightarrow$$ volume fraction of the conducting phase



P. F. Carcia, , A. Suna, and W. D. Childers, J. Appl. Phys. **54**, 6002 (1983)

M. Tamborin, S. Piccinini, M. Prudenziati, and B. Morten, Sensors and Actuators A **58**, 159 (1997)

- → According to the value of x, TFRs can be good or bad conductors
- → below a critical concentration x_c, TFRs become insulators
- → x_c depends upon the particular TFR
- → for $x \rightarrow x_c$ the resistance follows a power law of the form

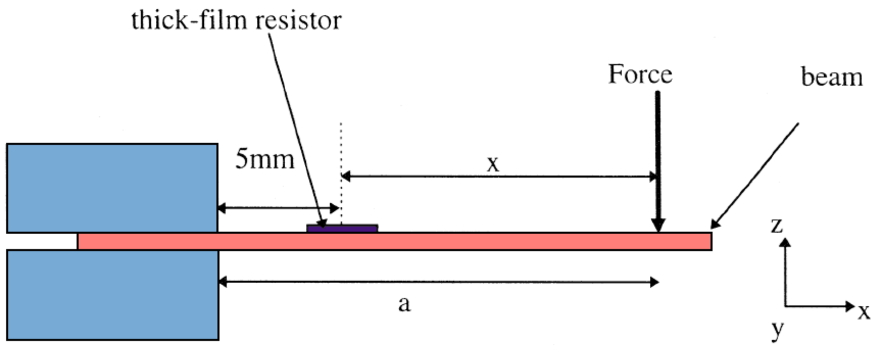
$$R \cong R_0(x-x_c)^{-t}$$

which indicates <u>percolative behavior</u>

Thick-film resistors 4/4 - piezoresistivity

The piezoresistive effect is the change of resistivity ρ upon a mechanical applied strain ε :

$$R_i = R^0_i + R^0_i \sum_j K_{ij}\, \varepsilon_j \qquad K_{ij} = \frac{d\ \ln(R_i)}{d\ \varepsilon_j} \cong \frac{\Delta R_i}{\varepsilon_j R_i}$$



cantilever beam

$K_{xx}=K_L$: longitudinal gauge factor

$K_{yx}=K_T$: transverse gauge factor

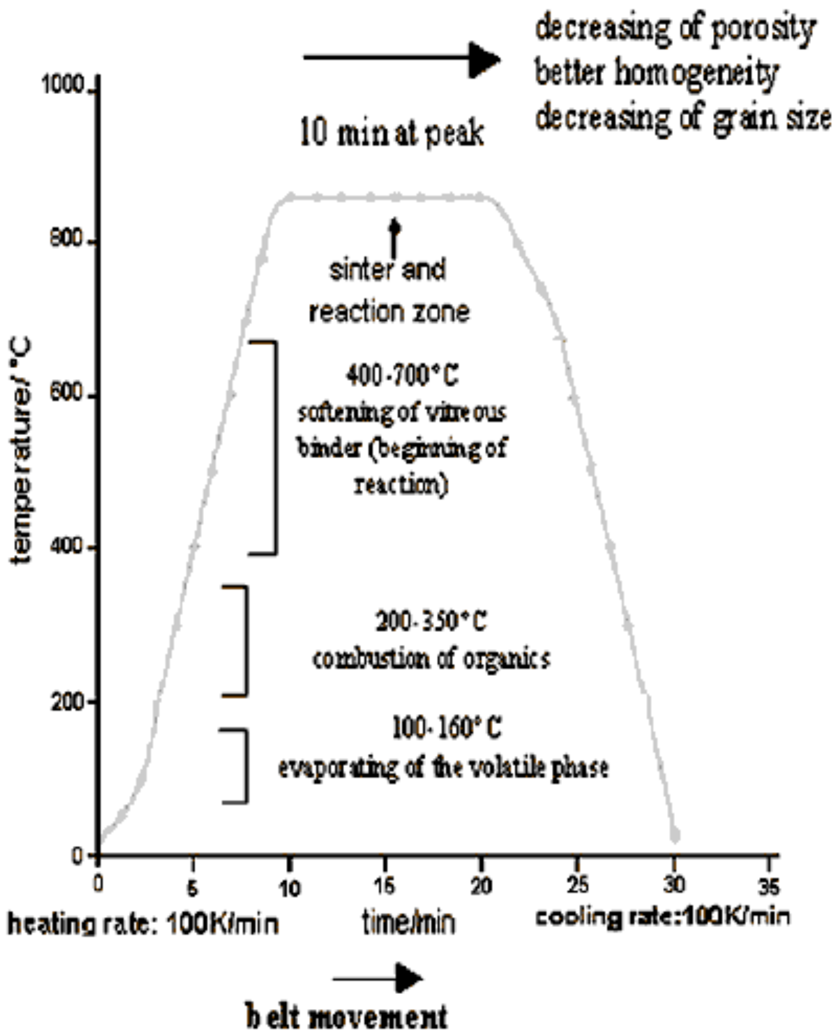
$$K = \frac{\Delta R}{\varepsilon R} = \frac{\Delta \rho}{\varepsilon \rho} + \text{geometric contribution}$$

The piezoresistive factor

$$\Gamma = \Delta\rho/\rho\varepsilon$$

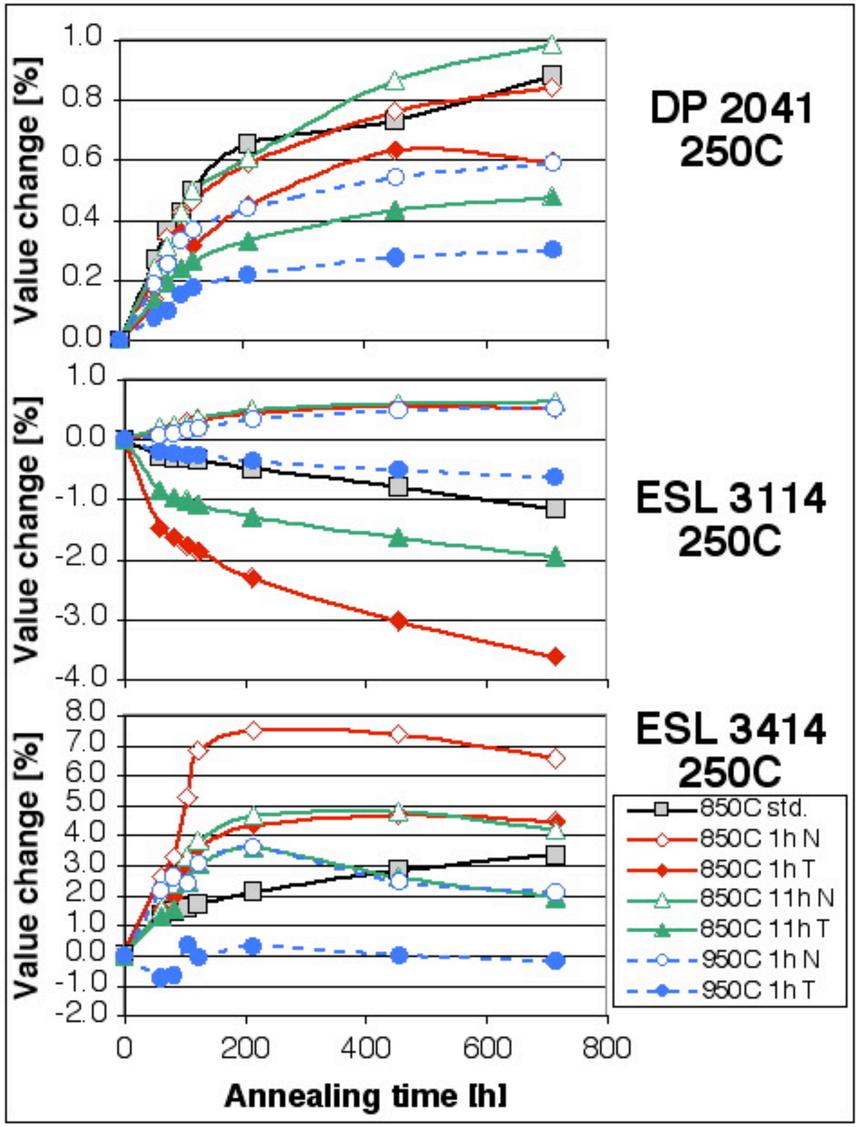
can be as high as $\Gamma \approx 30$

Thick-film resistors (TFRs): standard firing conditions



- **Temperature**: 850°C peak - too high for many substrates
- **Environment**: air - strongly oxidising conditions
- **Substrate**: alumina - very inert, ca. 7 ppm/K

Thick-film resistors (TFRs): stability



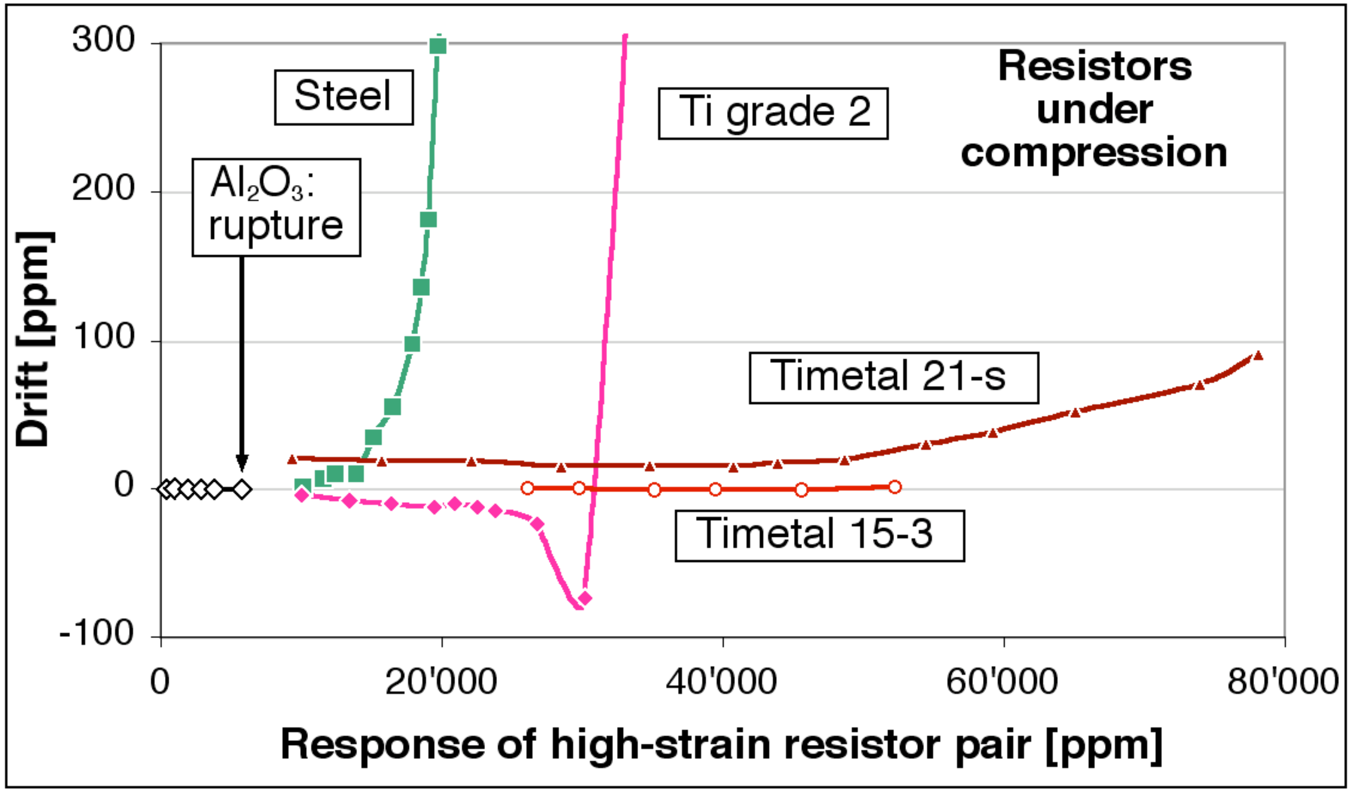
- 10 kOhm compositions:
  - DP 2041 = standard
  - ESL 3114 = 630°C firing, for porcelain enamelled steel
  - ESL 3414 = 850°C, high gauge factor
- Poor stability of ESL 3414
- Good stability of ESL 3114

Vionnet & al., 2004

N = furnace cool after firing

T = quenched after firing

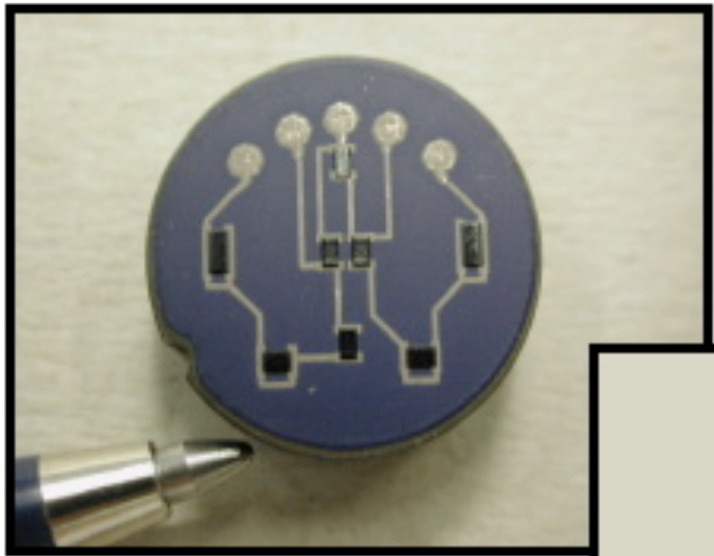
Thick-film resistors (TFRs): high piezoresistive response

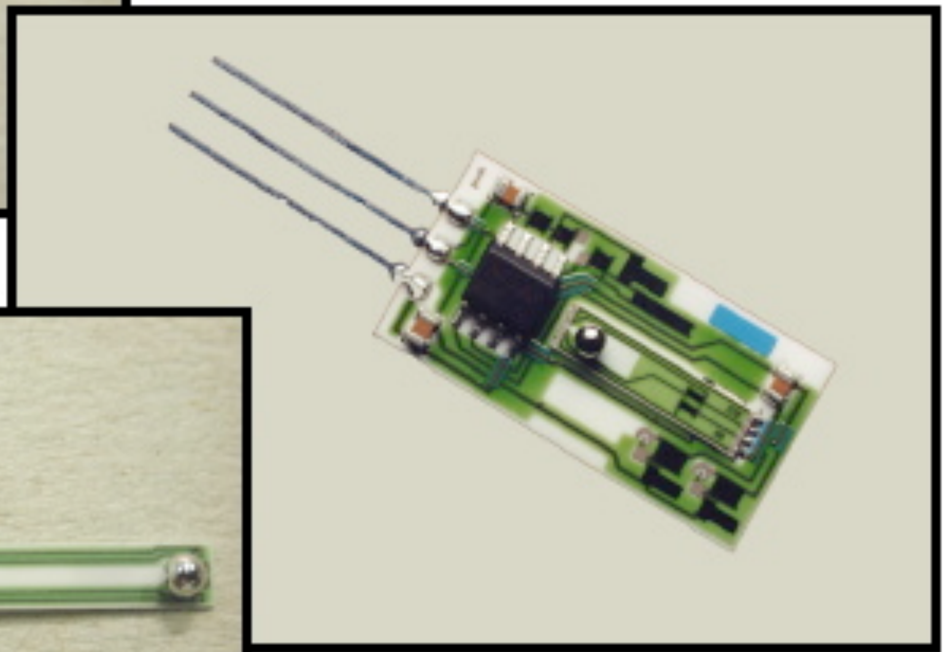


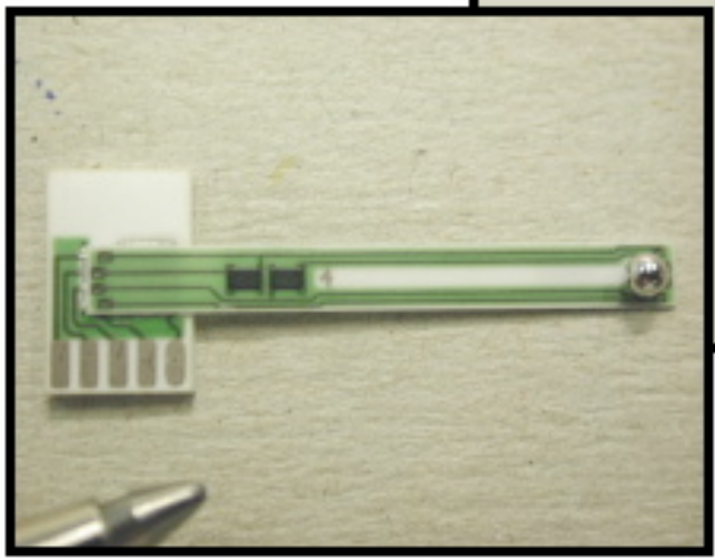
Jacq & al., 2004

- Design response on alumina : 0.3%
- Ultra high response possible: > 5%!
- Not practical: rapid oxidation of Ti & Ti alloys above 600°C - **need ≤ 600°C system!**

Applications: piezoresistive force & pressure sensors





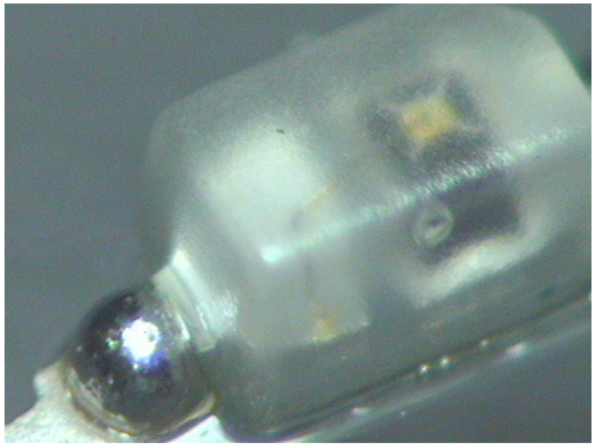


Applications: low-temperature thick-films

- High heat dissipation electronics - AlN*, Al
- Heaters - steels*, Al
- Rugged & inexpensive force & pressure sensors - metals
- Electronics on displays - glass
- (Electronics on polymer - PCB, etc.)

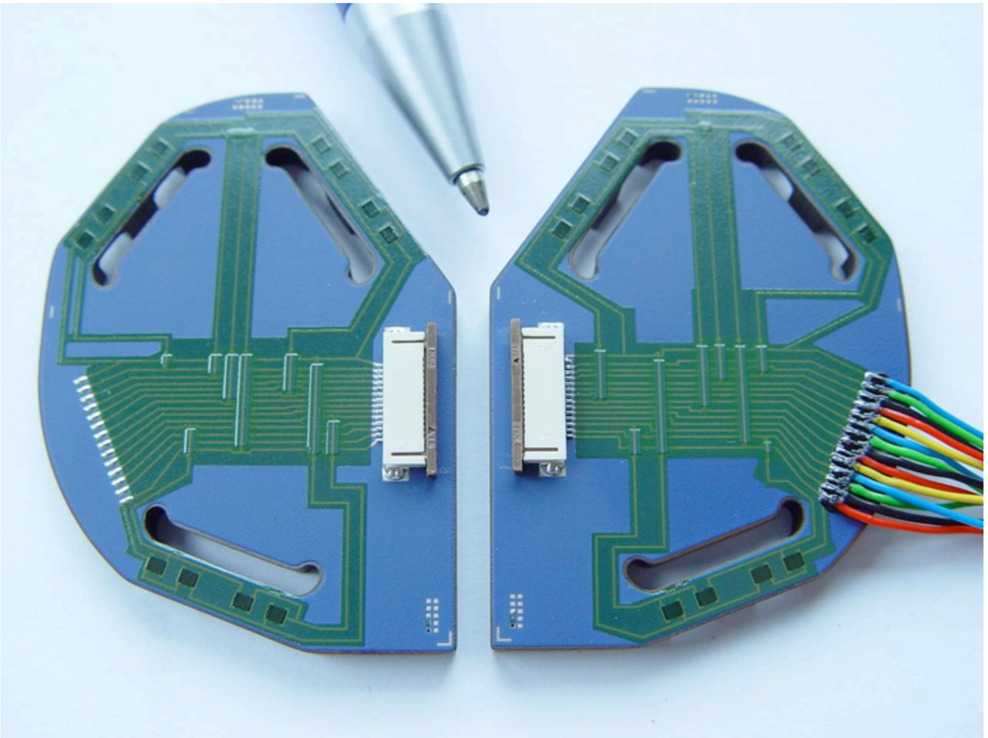
* Commercially available

Thick-film pressure sensor on steel, Huba Control DT 510

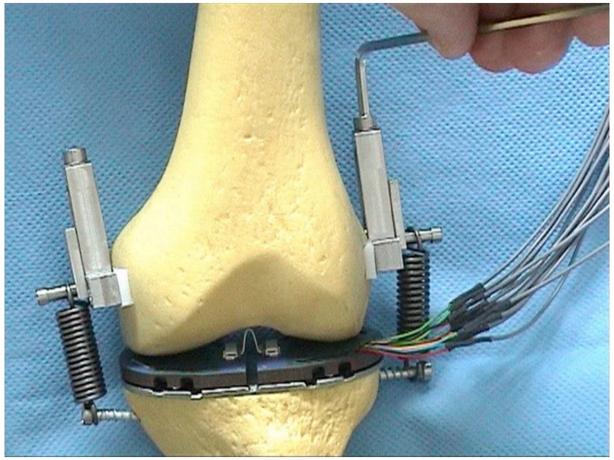


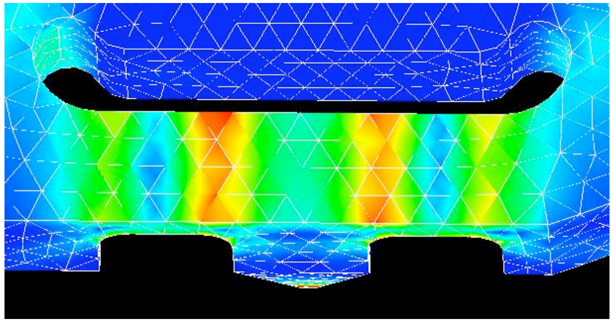
LED on glass thick-film circuit

Applications: a knee force sensor



Crottet & al., 2004





- ❑ Two sides with 3 independent sensing bridges / side
- ❑ Measurement of force & XY position on each side
- ❑ Determination of force and moments
- ❑ Steel sensing body

Applications: temperature limitations and their causes

Substrate	Max. temp. [°C]	Limiting factor
glass	550…650	deformation
Al alloys	500…630	melting
stainless steel	500…650*	softening
martensitic steel	ca. 700	transformation
tool steel & Ti	ca. 600	oxidation
polymer	ca. 300	decomposition

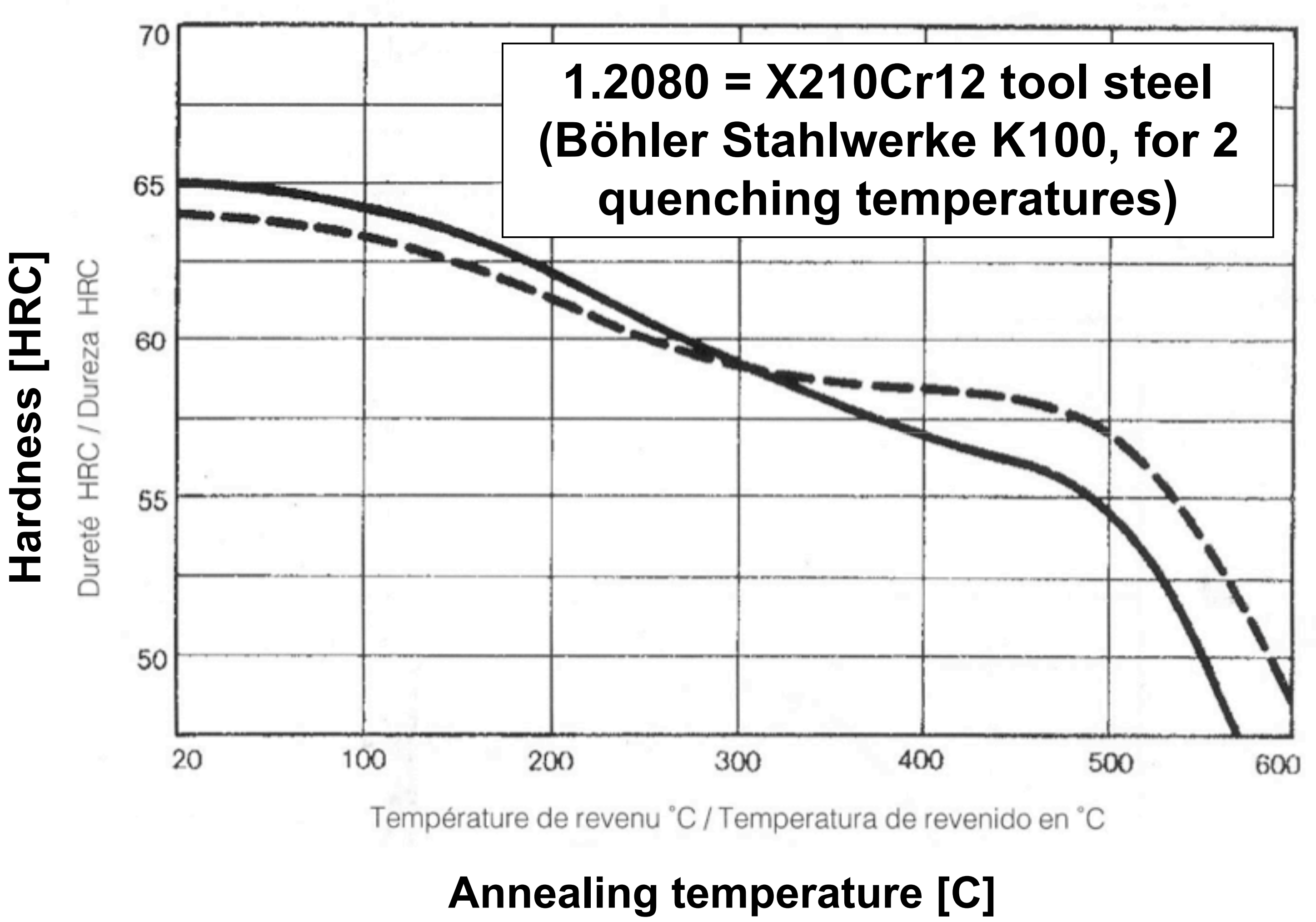
→ Systems in the 500…650°C range are interesting!

* For high performance

Steel - issues

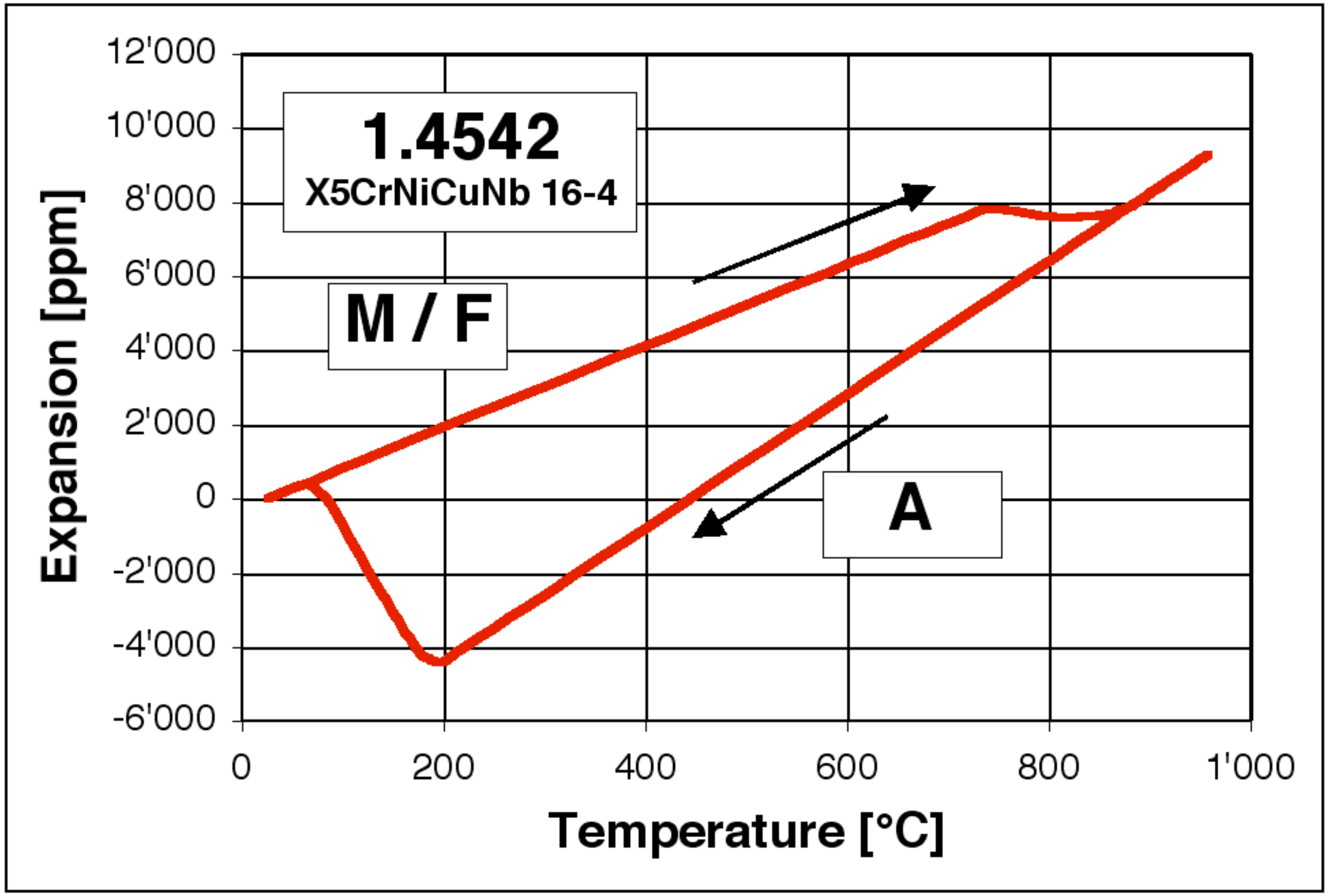
- ✓ **Oxidation** - most stainless steels have sufficient oxidation resistance for the standard thick-film process.
- ? **Adherence of dielectric** - many commercial dielectric compositions available - Co as adhesion promoter. Low-temperature systems?
- ! **Softening** - the effect of cold work and/or heat treatment are essentially lost!
- ! **Martensitic transformation** - disruptive volume change => cracking of dielectric!

Steel - issues - softening at high temperature



→ 600…650°C = the limit for retention of high strength

Steel - issues - martensitic transformation



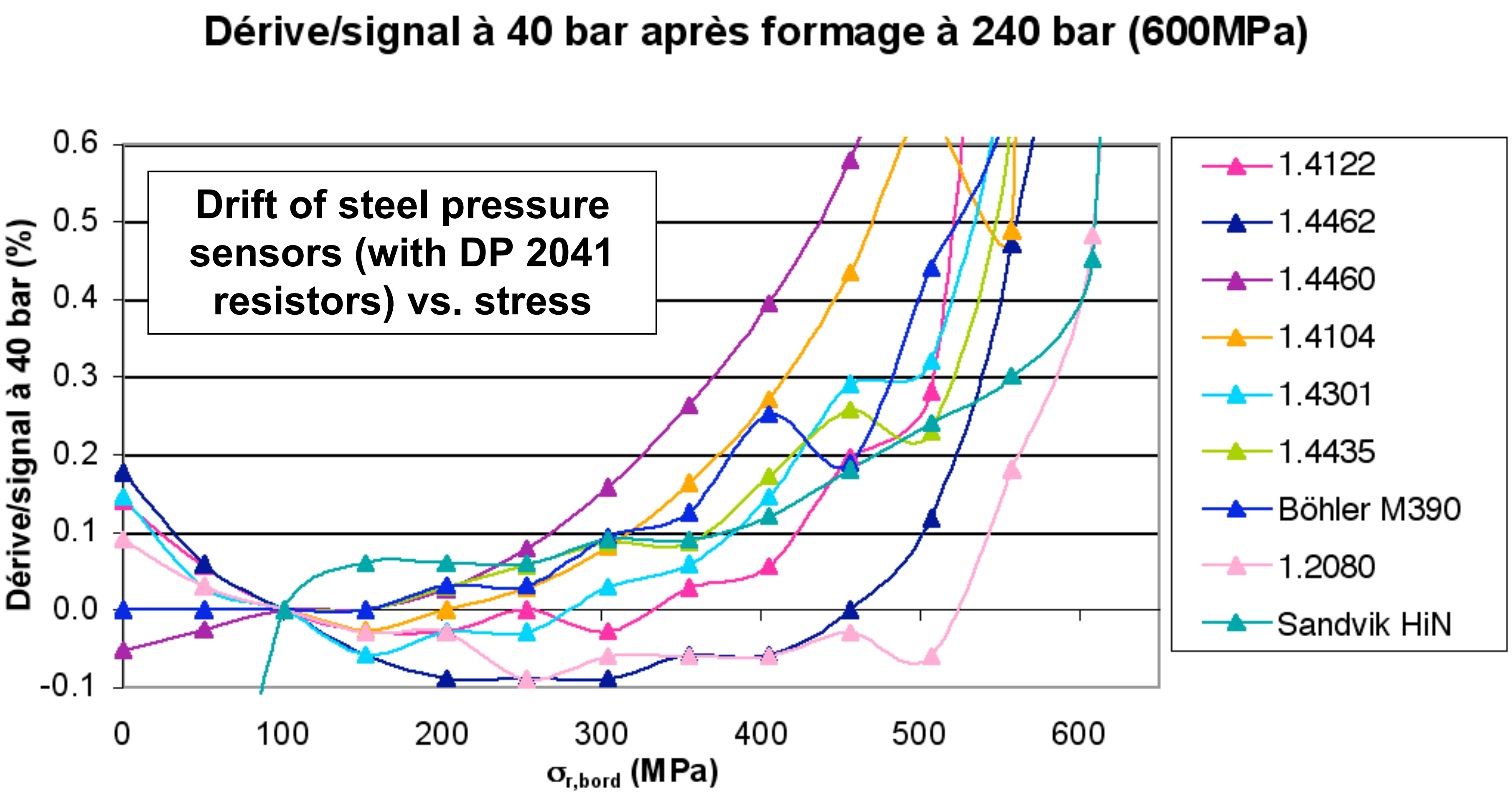
M = martensite
F = ferrite
A = austenite

→ Must avoid disruptive martensitic transformation!

→ Work below 700°C!

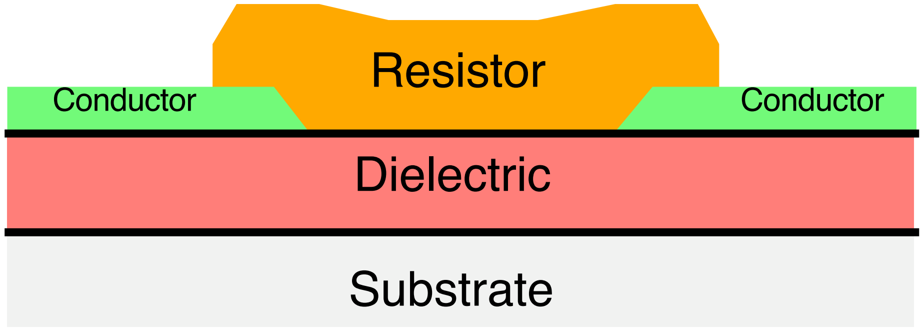
Vionnet & Maeder 2000

Steel - current thick-film pressure sensors



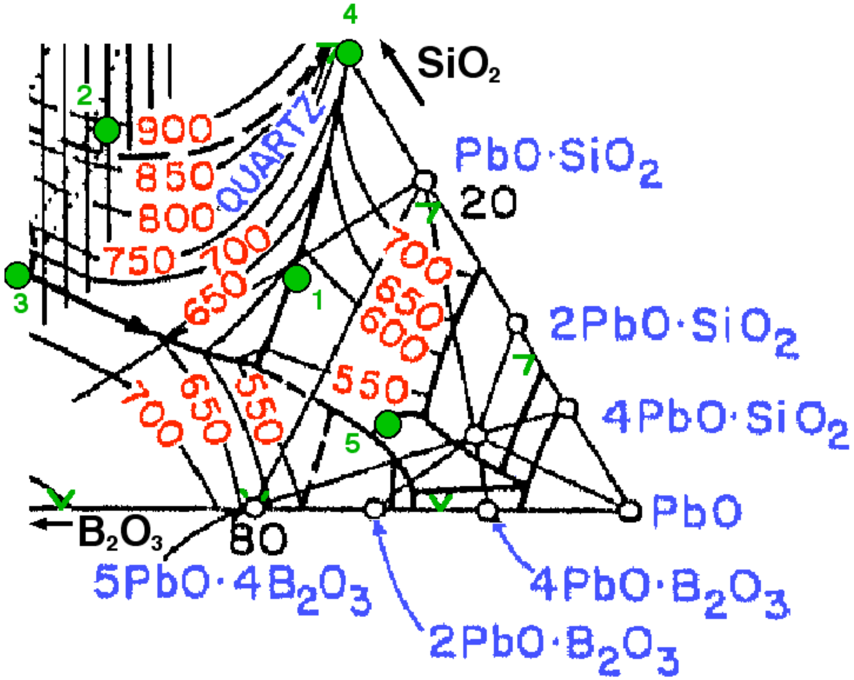
- ❑ Sufficient for rugged low-precision sensors
- ❑ High precision not possible due to softening

Low temperature - current status



- **Resistors** : 625°C nominal firing temperature (ESL 3114) - somewhat too high
- **Conductors** : commercially available at < 500°C
- **Glasses** : low-melting point glasses available, **but :**
- **Glasses are not stable** ⇒ infiltration of conductors & resistors
- **Need for better low-temp. resistors & dielectrics!**

Resistors - studied glass compositions

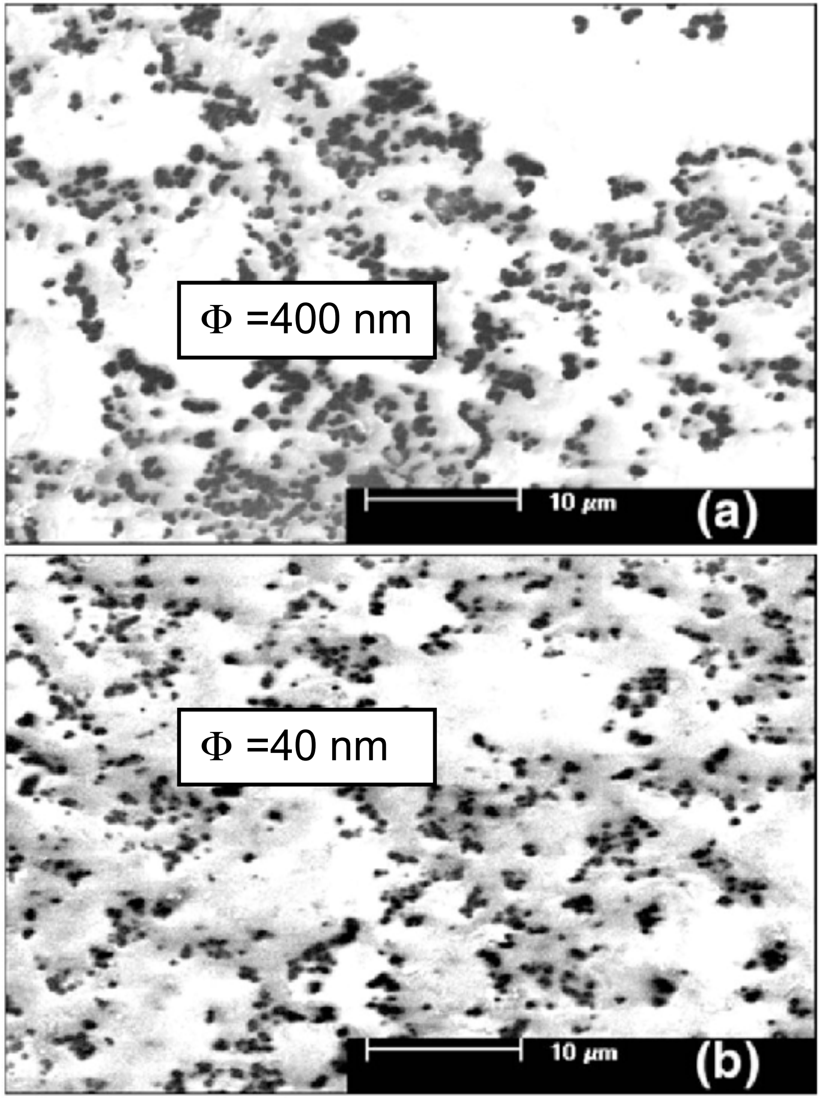


2-5% Al_2O_3 added to inhibit crystallisation

1. **PbO-SiO_2-B_2O_3, by weight 75–15–10%**
2. Standard (850°C firing) : 60–25–15%
3. Also often used : 60–15–25%
4. PbO-SiO_2 only : ca. 70–30–0%
5. Future work (<600°C) : 85–5–10% (TCE!)

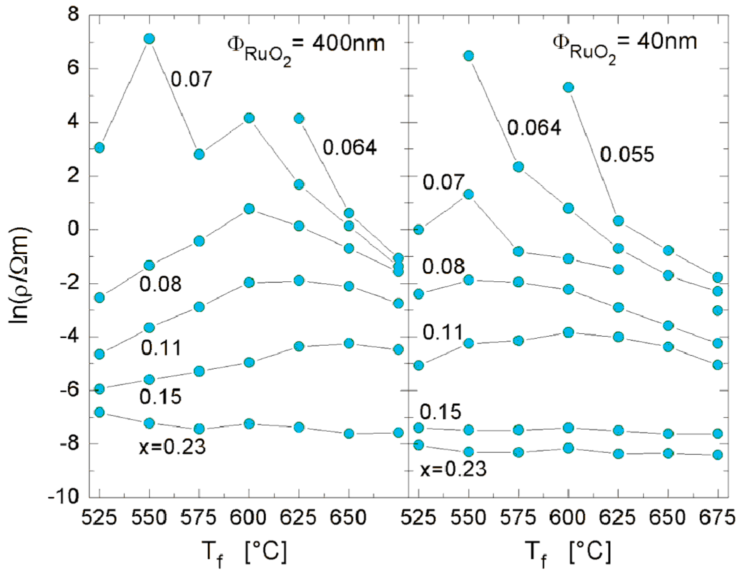
Preparation of RuO_2-based low-temperature TFRs

- Metallic phase: RuO_2 particles with diameter Φ =400 nm and Φ =40 nm
- Insulating phase: PbO (75% wt) -B_2O_3 (10% wt)-SiO_2 (15% wt)
- 2% of Al_2O_3 added to avoid possible crystallization
- Glass softening temperature Ts=460°C
- Organic vehicles: terpineol & ethyl cellulose
- Firing cycle: drying phase (10 min at 150 °C), plateau at various T_f for 15 min
- **Firing temperature: 525 to 675°C**

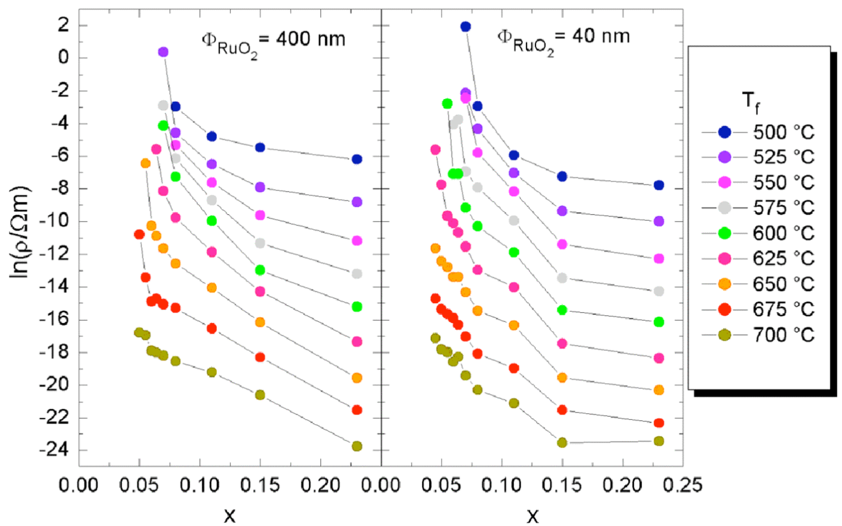


Effects of firing temperature T_f

The firing temperature T_f has important effects on TFRs transport properties

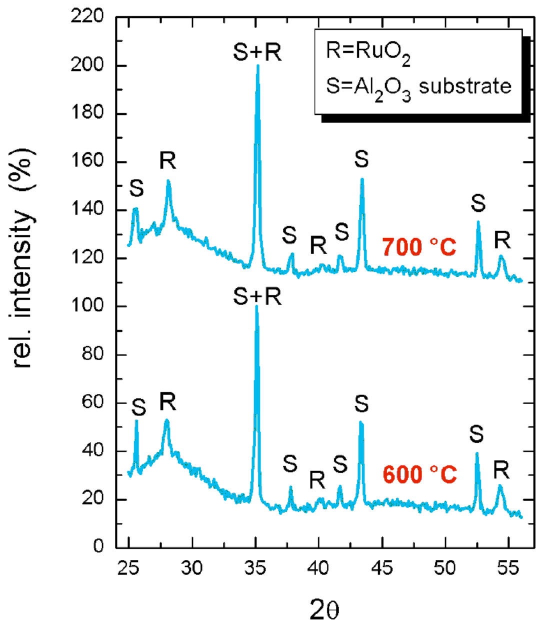


- → At moderate RuO_2 concentration x the resistivity displays a maximum
- → at low x the resistivity is monotonous
- → at very high T_f the resistivity is weak x dependent



- → At low T_f there is a clear percolative behavior
- → as T_f increases, the critical volume fraction x_c shift to lower values
- → at very high T_f there is no evidence of percolative transition (weak x dependence)

Microstructure & phases



→ X-ray analysis does not show extra peaks associated to possible formation of $Pb_2Ru_2O_6$

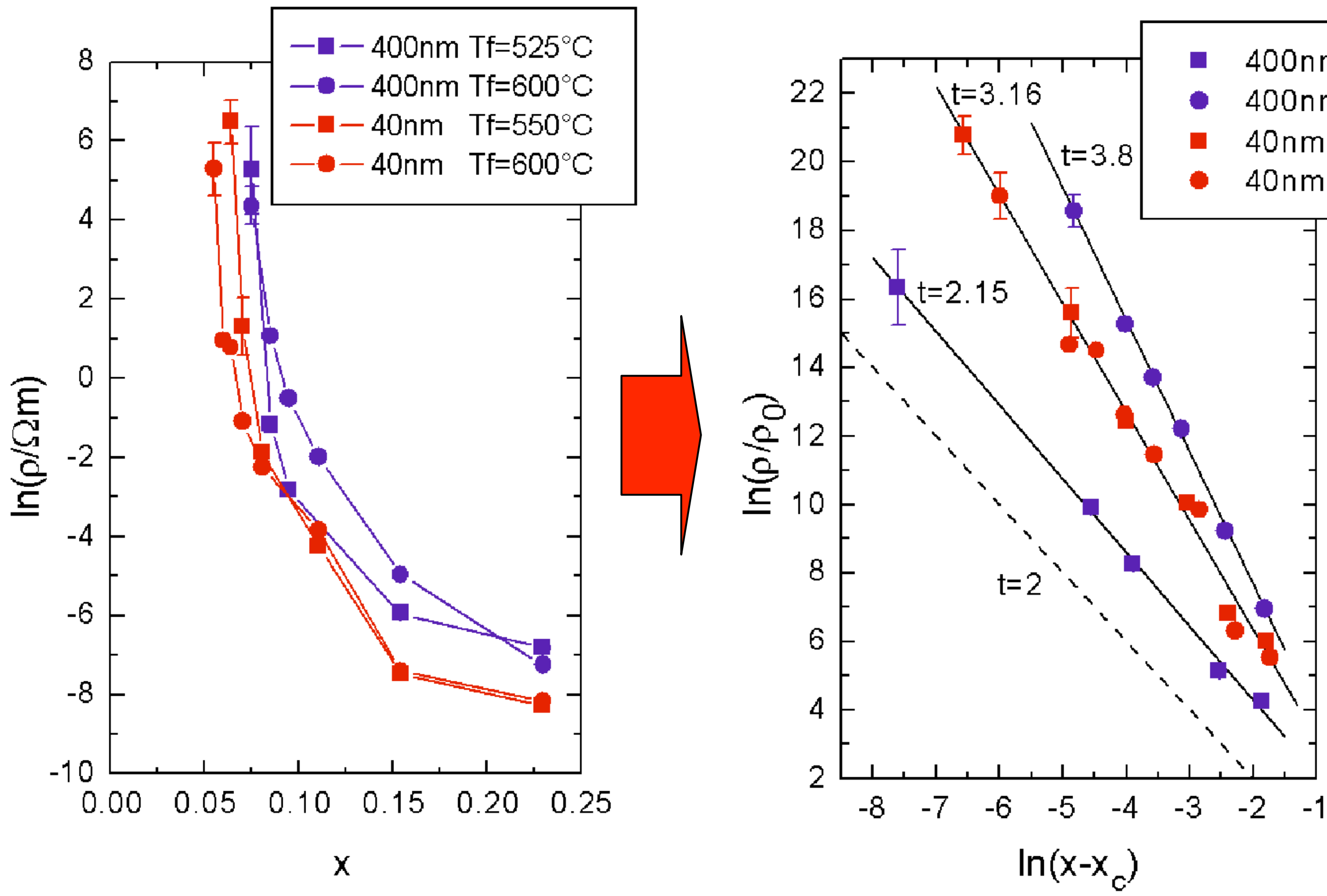
→ overfired samples (T_f=700 °C for 1h) display the same x-ray reflection peaks

→ there is no evidence for variation of the conducting phase concentration with T_f

Low T_f	Intermediate T_f	High T_f
the initial RuO_2 clusters are wetted by the glassy phase x_c is given mainly by the large RuO_2 clusters the glass starts to penetrate inside the clusters separating the original RuO_2 particles	the initial RuO_2 clusters are completely dissolved in the glass the percolation threshold is given by the small RuO_2 particles rather than the large RuO_2 clusters x_c is decreased	the glass viscosity is so low that RuO_2 particles may concentrate in the bottom of the TFR (precipitation) in this case the conducting phase is macroscopically inhomogeneous

Percolation properties

T_f and RuO_2 grain size affect also the percolation properties of TFRs



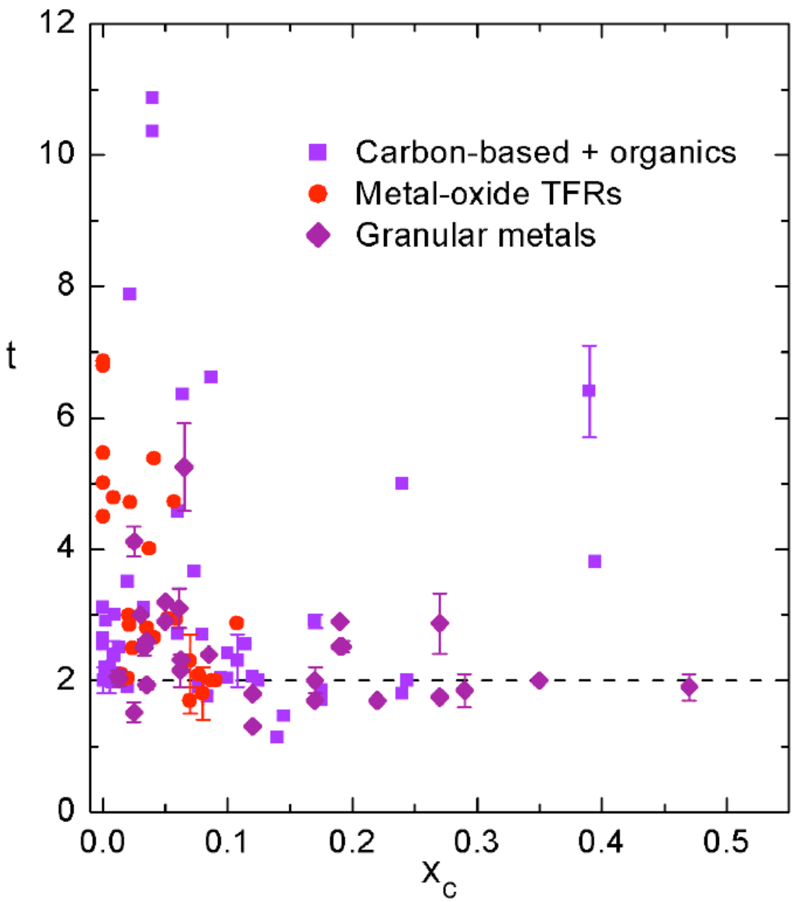
$\rho \cong \rho_0(x-x_c)^{-t}$

critical percolative behavior close to the insulator transition

the critical exponent is $t \geq 2$

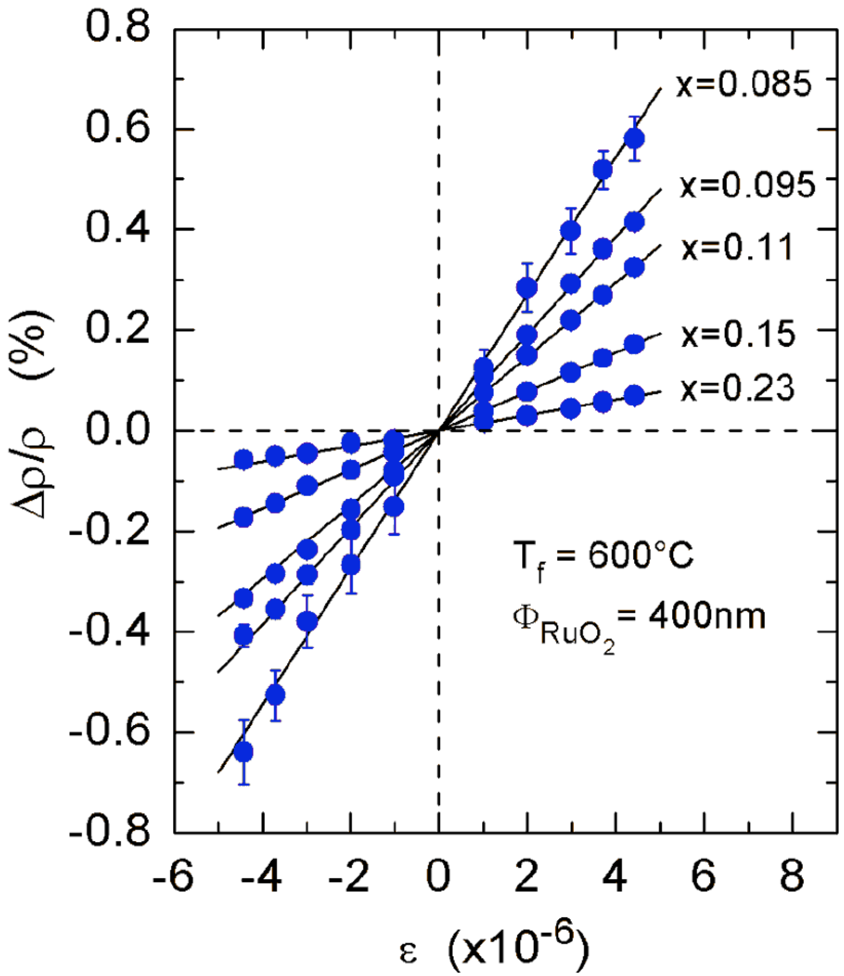
Percolation properties

$$\rho \cong \rho_0 (x - x_c)^{-t}$$



- The critical behavior is observed for various conductor-insulator composites
- about 50% of the measured exponents t are close to **t=2** that is the value predicted by conventional percolation theory
- deviations from t=2 indicate non-universal behavior of transport
- TFRs may have t=2 or t>2 depending on the fabrication procedures
- The origin of non-universal behavior (t>2) is not fully understood

Effect of percolation on piezoresistive properties

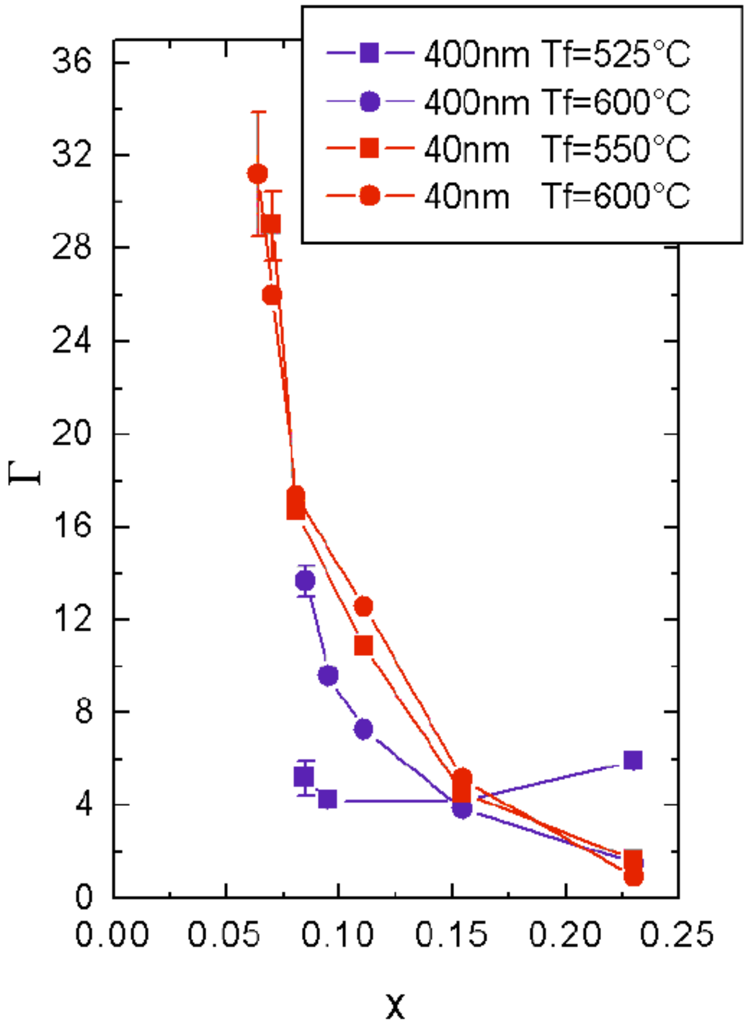


- → The effect of strain is **linear and symmetric**
- → there is no evidence of false signals due to possible cracks or other strain faults
- → as the RuO_2 concentration x lowers, the resistivity change $\Delta\rho/\rho$ increases
- → the piezoresistive factor

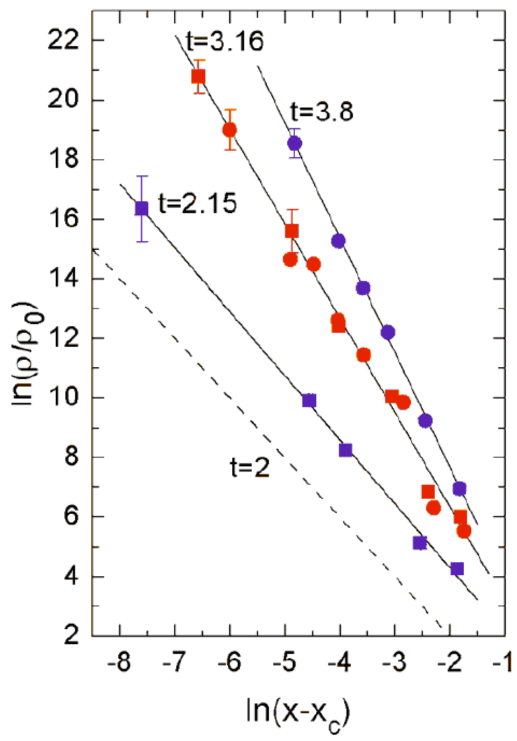
$$\Gamma = d\ln(\rho)/d\varepsilon$$

can be extracted from the linear fits of $\Delta\rho/\rho$ versus ε

Effect of percolation on piezoresistive properties



- → With the exception of the 400nm T_f=525°C series, the piezoresistive factor Γ increases monotonously as x decreases
- → Γ appears to **diverge** at the same critical concentration x_c for which $\rho \rightarrow \infty$

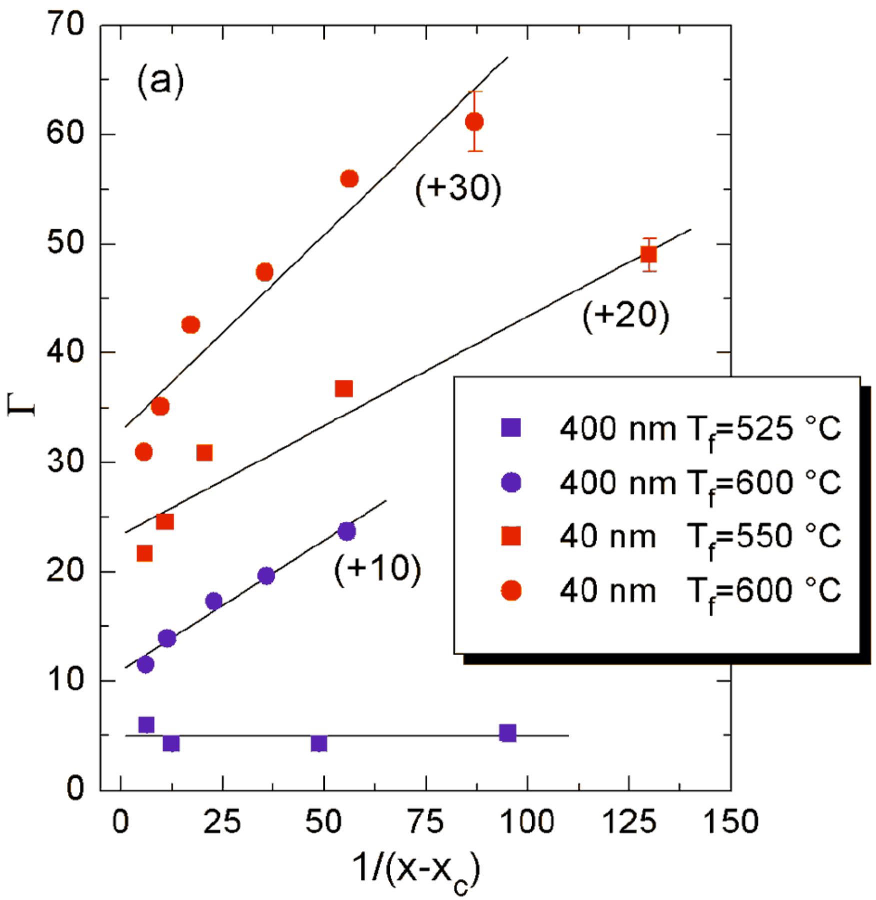


It appears that there is a **correlation** between diverging Γ and non-universal behavior of transport (t>2)

Effect of percolation on piezoresistive properties

The divergence of Γ at x_c could be maybe due to a strain effect on x

$$\Gamma = \frac{d\ln(\rho)}{d\varepsilon} = \Gamma_0 + A\,t\,x/(x-x_c) = K_1 + K_2/(x-x_c)$$



→ The fits to the 40 nm series are bad

→ it is not clear why the 400 nm T_f=525 °C series should not diverge

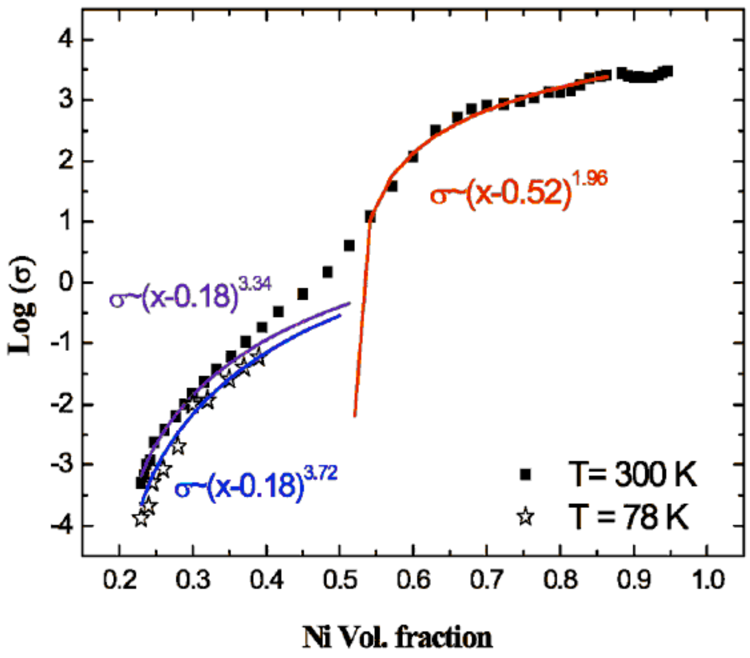
→ x is just a measure of the inter-grain junctions, if $dx/d\varepsilon \neq 0$ then an applied strain would break the junctions… but the variation of resistivity is linear in ε

→ a different explanation should be sought

Effect of percolation on piezoresistive properties

RuO_2 TFRs are tunneling-percolation systems: current flows through the sample via tunneling hopping between RuO_2 adjacent particles

Example: Ni-SiO_2 cermets



I. Balberg *et al.*, Int. J. Modern Phys. B **18**, 2091 (2004)

- → At high metal concentrations the conducting particles form a cluster of touching elements
- → there is a first (geometrical) percolative transition when the cluster of touching particles do no longer span the entire sample
- → at lower concentrations, current flows via inter-particle tunneling
- → there is a second (lower) percolation transition of tunneling junctions

Effect of percolation on piezoresistive properties

The tunneling-percolation theory predicts that the DC exponent t depends on the mean **tunneling distance a and the tunneling decay ξ**

$$t = 2 \quad \text{if} \quad \upsilon + 2a/\xi < 2$$

$$t = \upsilon + 2a/\xi \quad \text{if} \quad \upsilon + 2a/\xi > 2$$

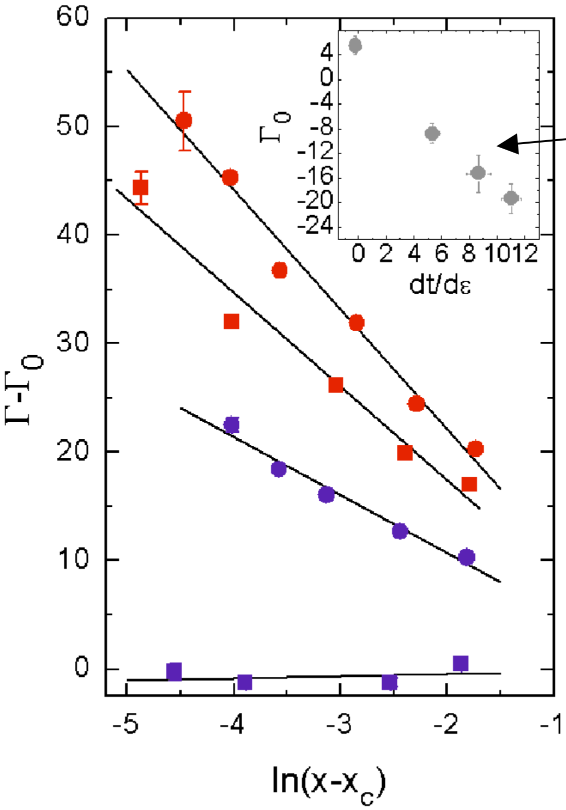
I. Balberg, Phys. Rev. Lett. **59**, 1305 (1987)

where υ = 0.88 is the correlation length exponent (a geometrical quantity)

An applied strain ε affects the tunneling distance a $\rightarrow$ a(1+ ε)

$$\rho \cong \rho_0 (x-x_c)^{-t}$$

$$\Gamma = \frac{d\ln(\rho)}{d\varepsilon} = \Gamma_0 - (dt/d\varepsilon)\ln(x-x_c)$$



$\Gamma_0 \propto$ -dt/dε

Effect of percolation on piezoresistive properties

A1 : 400 nm, T_f=525 °C

A2 : 400 nm, T_f=600 °C

B1 : 40 nm, T_f=550 °C

B2 : 40 nm, T_f=600 °C

	A1	A2	B1	B2
x_c	0.0745	0.0670	0.0626	0.0525
t	2.15	3.84	3.17	3.15
Γ_0	5.5±1.5	-8.8±1.6	-15.3±3	-19.3±2.4
dt/dε	-0.2±0.4	5.4±0.5	8.7±0.9	11.0±0.7

→ The tunneling-percolation theory explains why when t> 2 the piezoresistivity diverges at x_c

→ the logarithmic divergence fits well with the experimental data

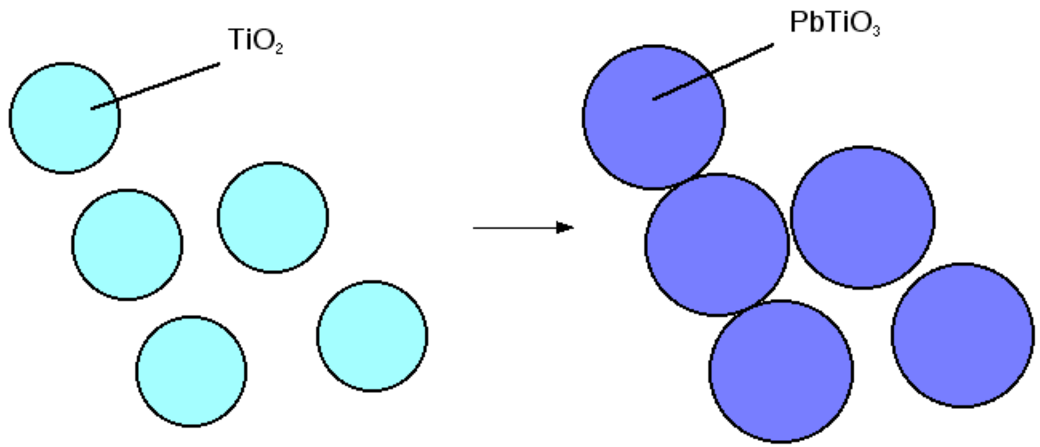
→ Monte Carlo calculations confirm that $\Gamma_0 \propto -dt/d\varepsilon$

Resulting understanding of TFR physics

- Besides their applicative advantages, low-temperature systems allow better isolation of physical properties
- Transport properties of TFRs are strongly affected by fabrication variables such as the firing temperature T_f and conductor volume concentration x
- The percolating behavior of TFRs depends upon T_f (the crititcal concentration x_c lowers as T_f is enhanced)
- TFRs may display non-universal behavior of critical transport
- For non-universal TFRs, the piezoresistivity response diverges at x_c
- The tunneling-percolation theory provides a consistent explanation of the piezoresistive divergence

Dielectrics: stabilisation by TiO_2

TiO_2 particles & lead glass

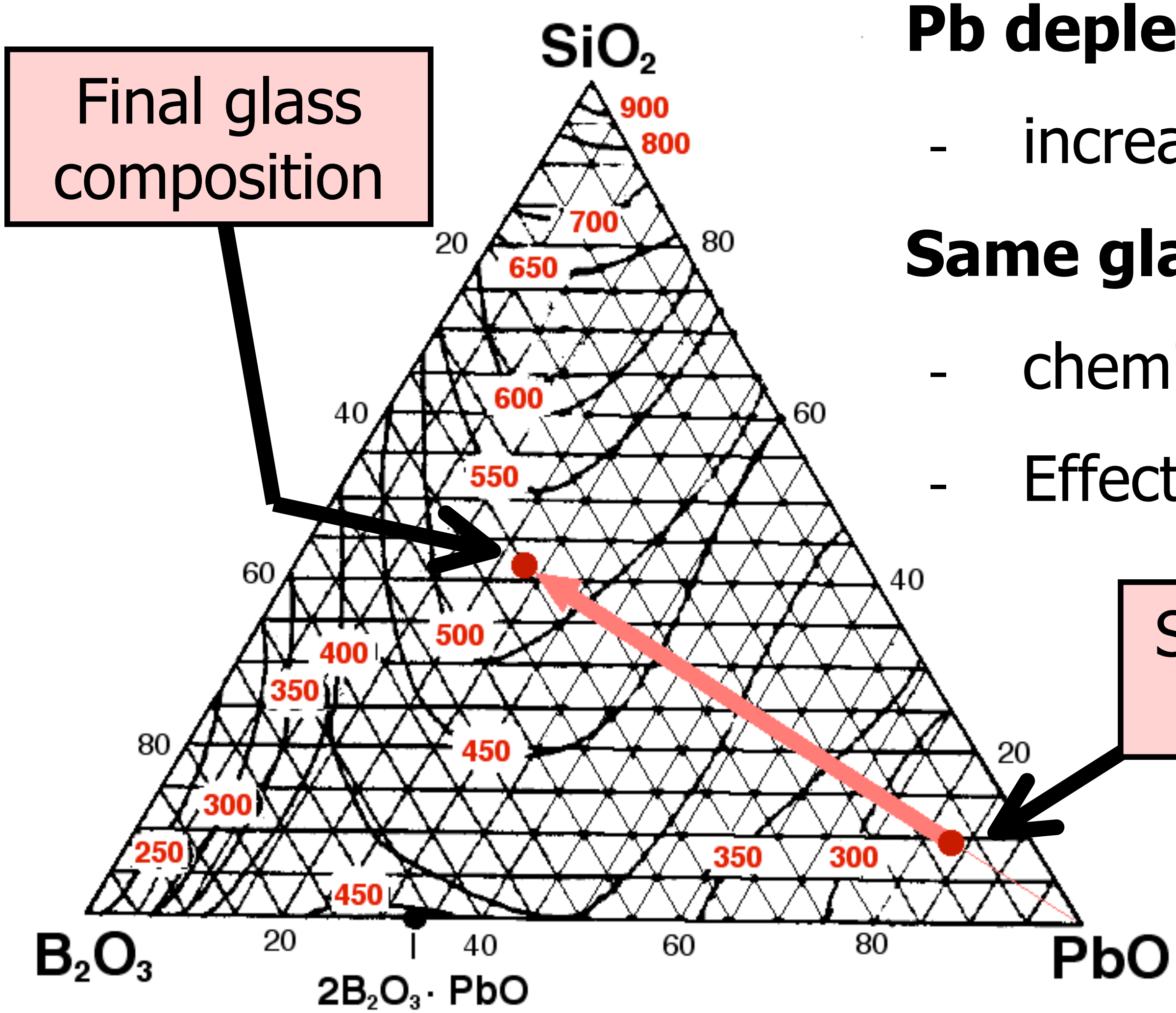


PbO (glass) + TiO_2 (nano grains) ⟹ $PbTiO_3$

Stabilisation by:

1. **Pb depletion in glass** and
2. **increase in filler volume**

Dielectrics: stabilisation by TiO_2



Pb depletion

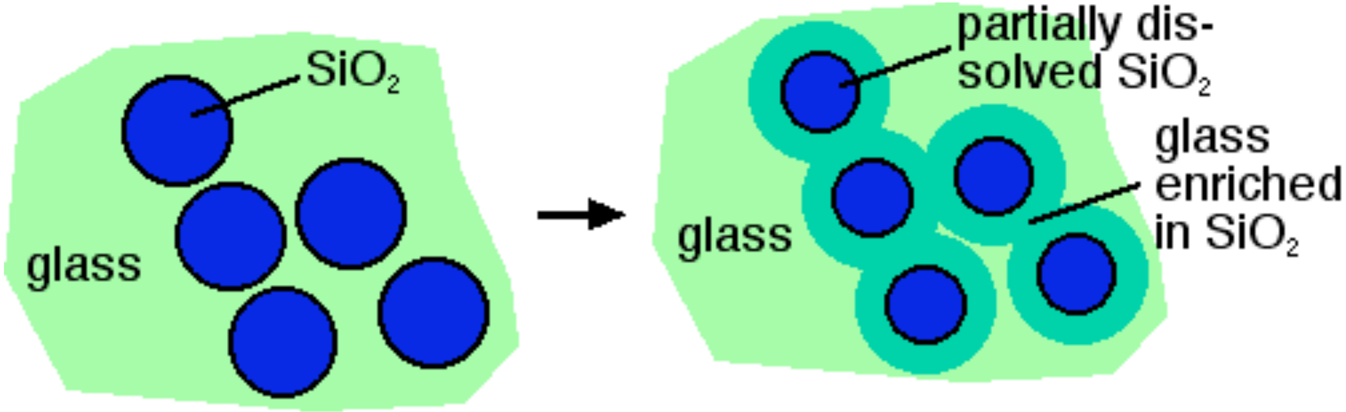
- increase of melting point

Same glass as resistors

- chemical compatibility
- Effect of TiO_2?

Dielectrics: stabilisation by SiO_2

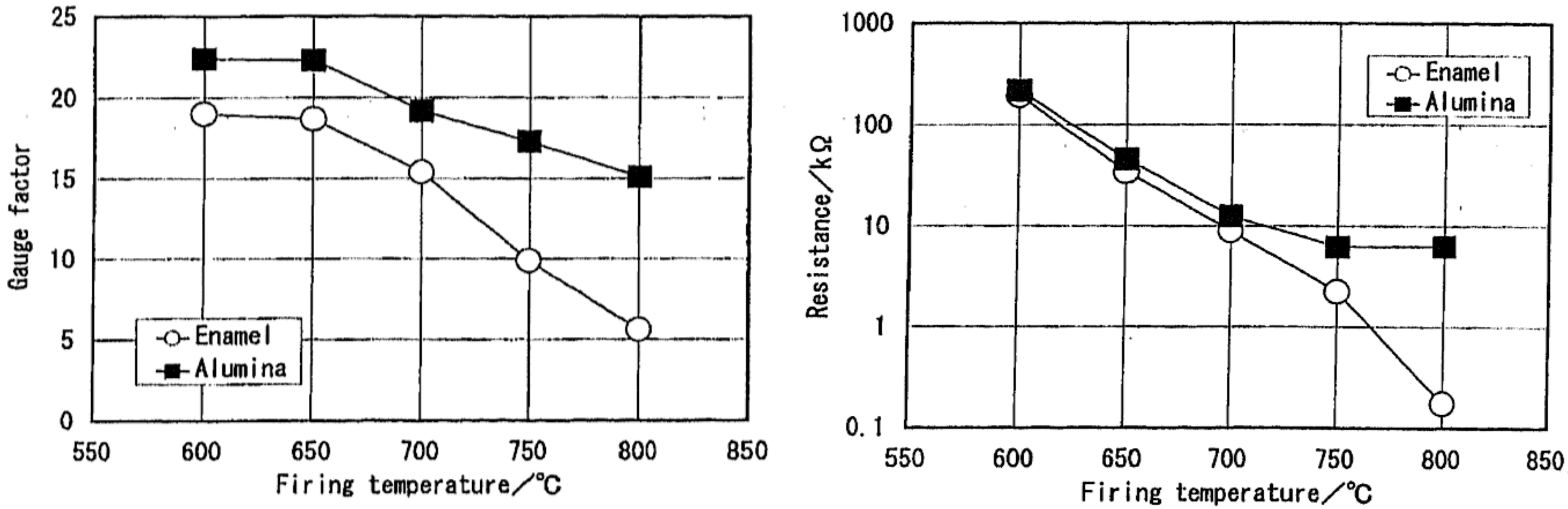
SiO_2 particles & low-temp. glass



glass + SiO_2 → SiO_2 - rich glass

- Stabilisation by SiO_2 - enriched skeleton
- Effet on resistors?
- Could use inside resistors?

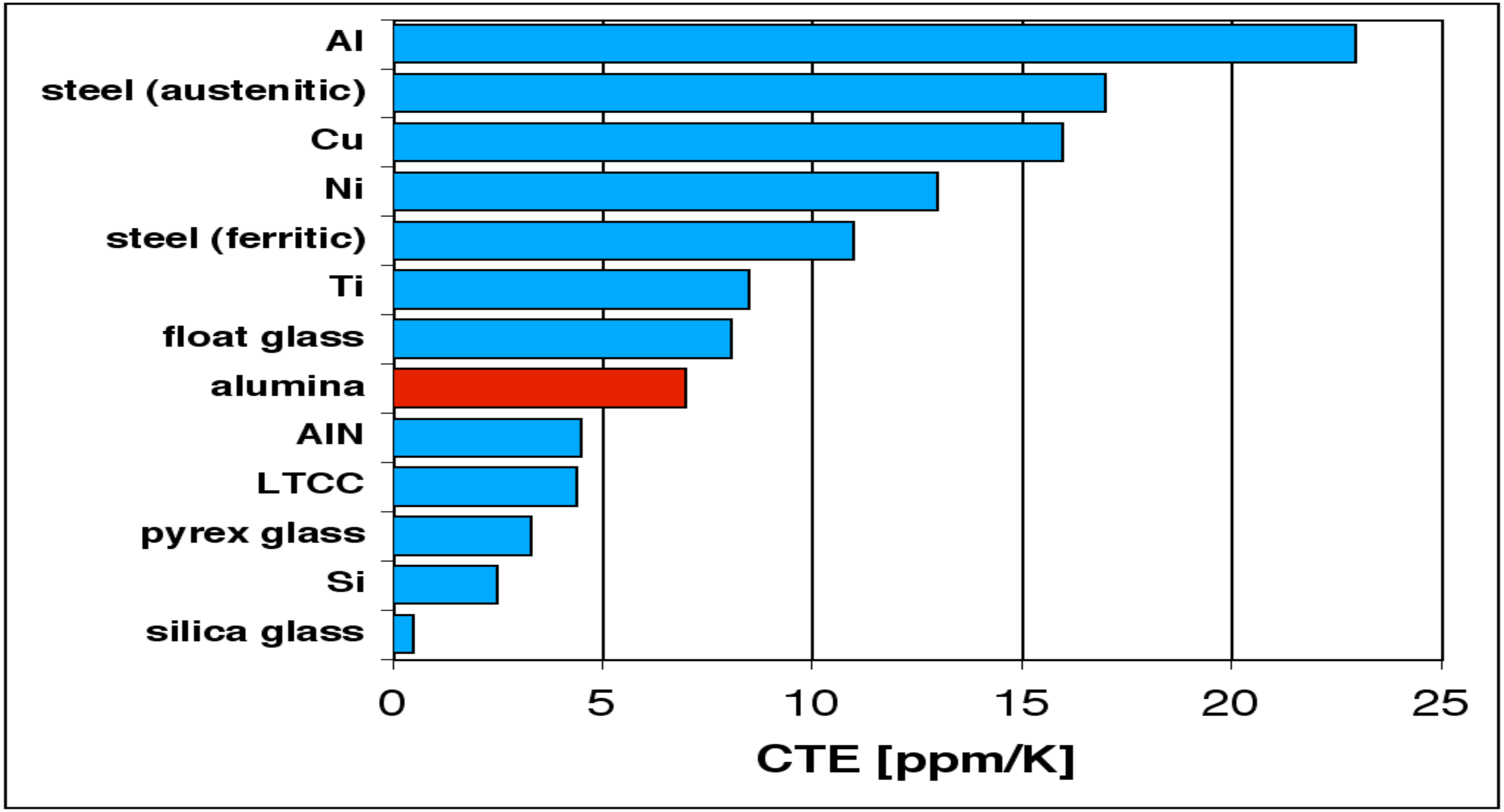
Dielectrics: effect on resistors



Hori et al., 1997

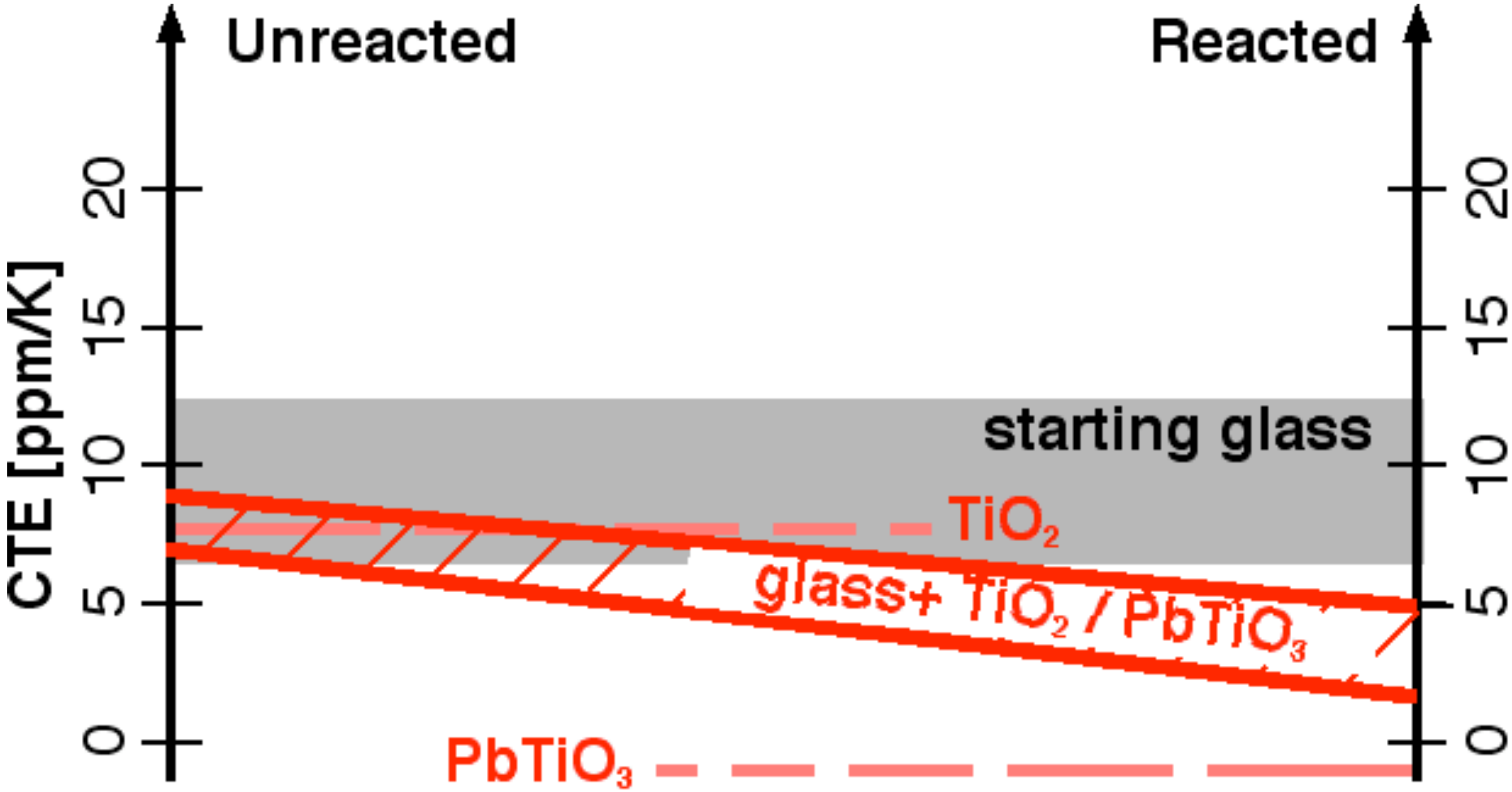
- Resistors on steel + enamel vs. alumina
- Strong reaction on enamel
- Alteration of properties

Thermal expansion matching: substrate materials



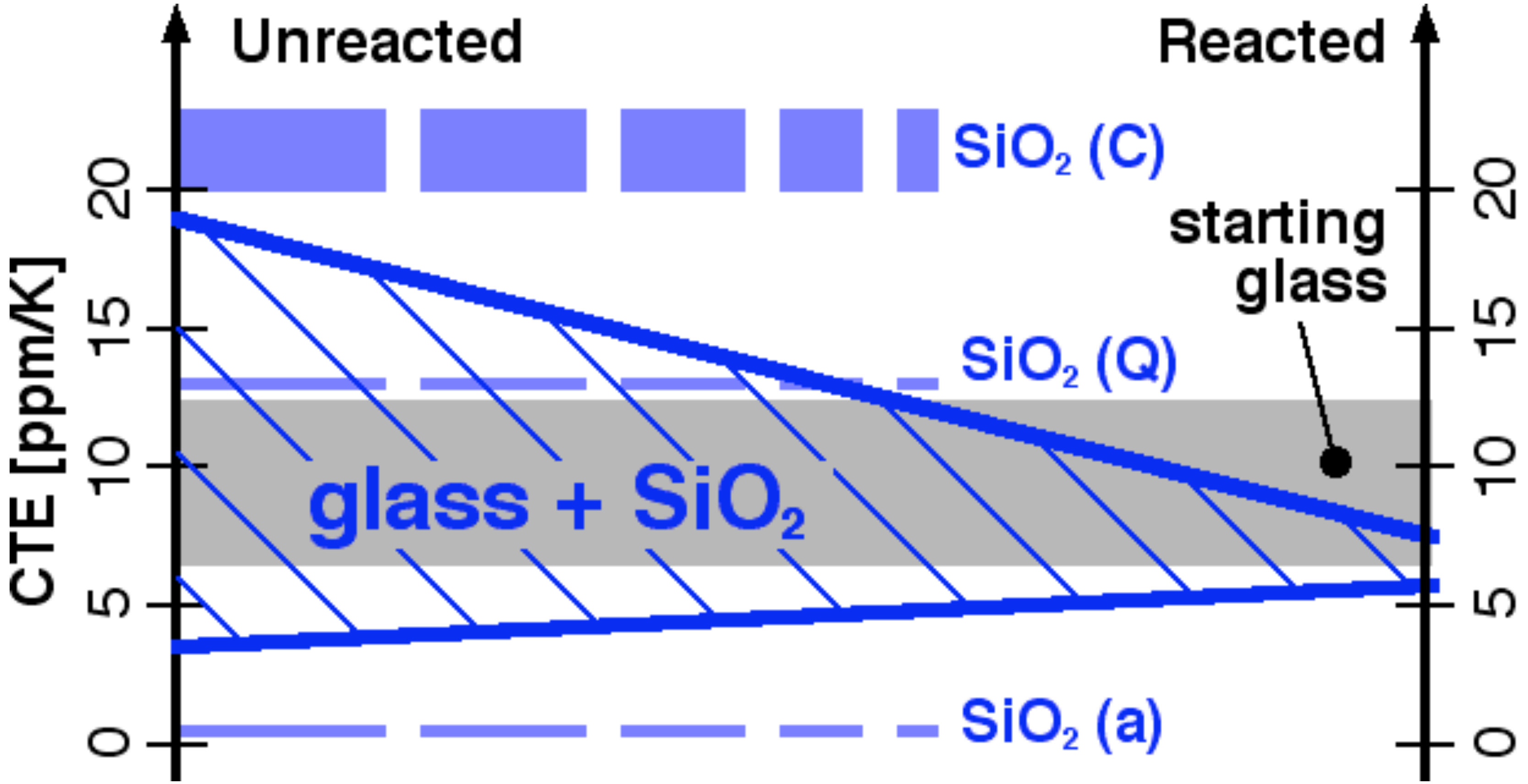
- Wide range of coefficients of thermal expansion (CTEs)
- Difficult to design generic systems

Thermal expansion matching: glass + TiO_2



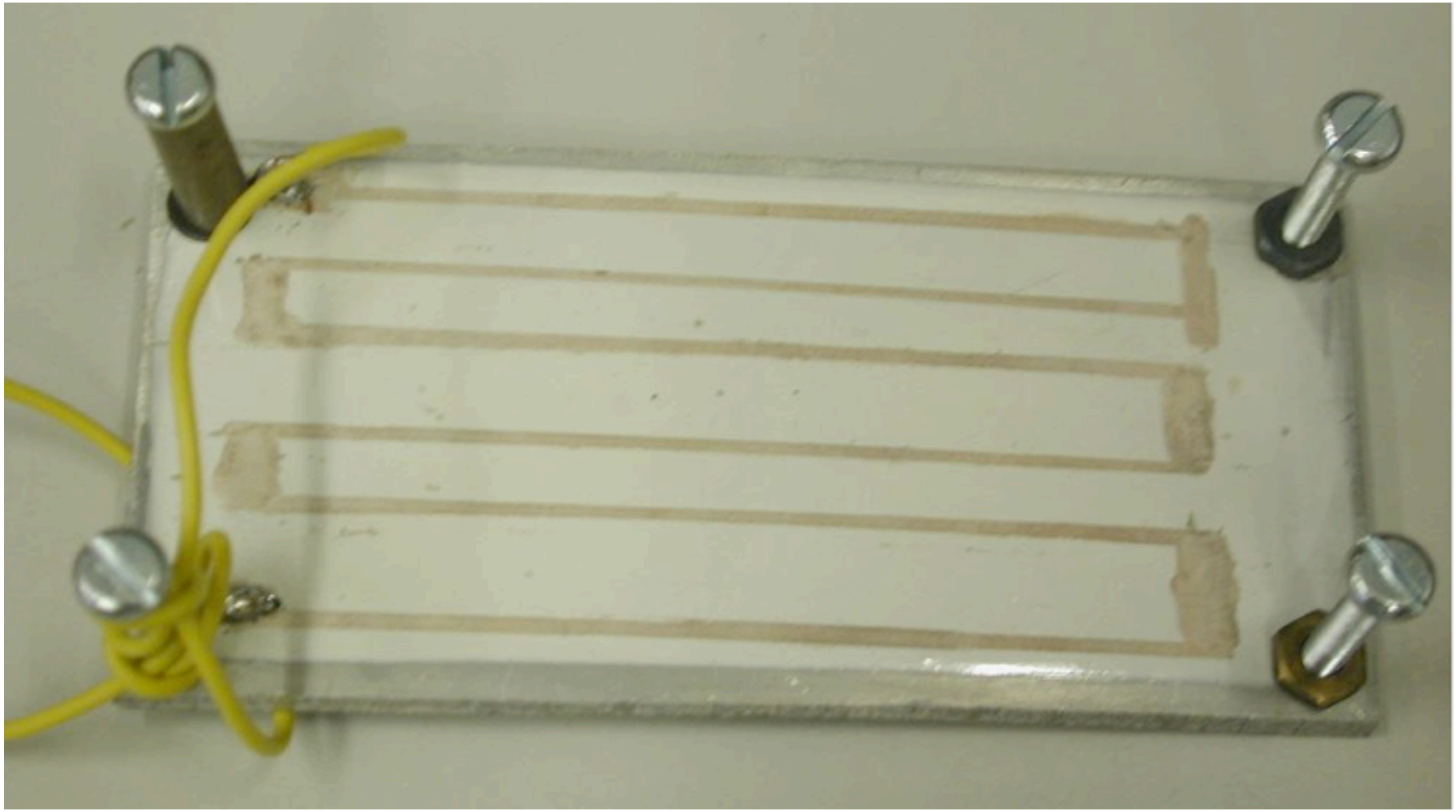
- For low CTE values
- $PbTiO_3$: CTE < 0 near room temperature

Thermal expansion matching: glass + SiO_2



- **Little reaction**: very wide range of CTE values possible due to different forms of SiO_2
- **Fully reacted**: OK for alumina, float glass & Ti

Application: prototype hot plate on Al

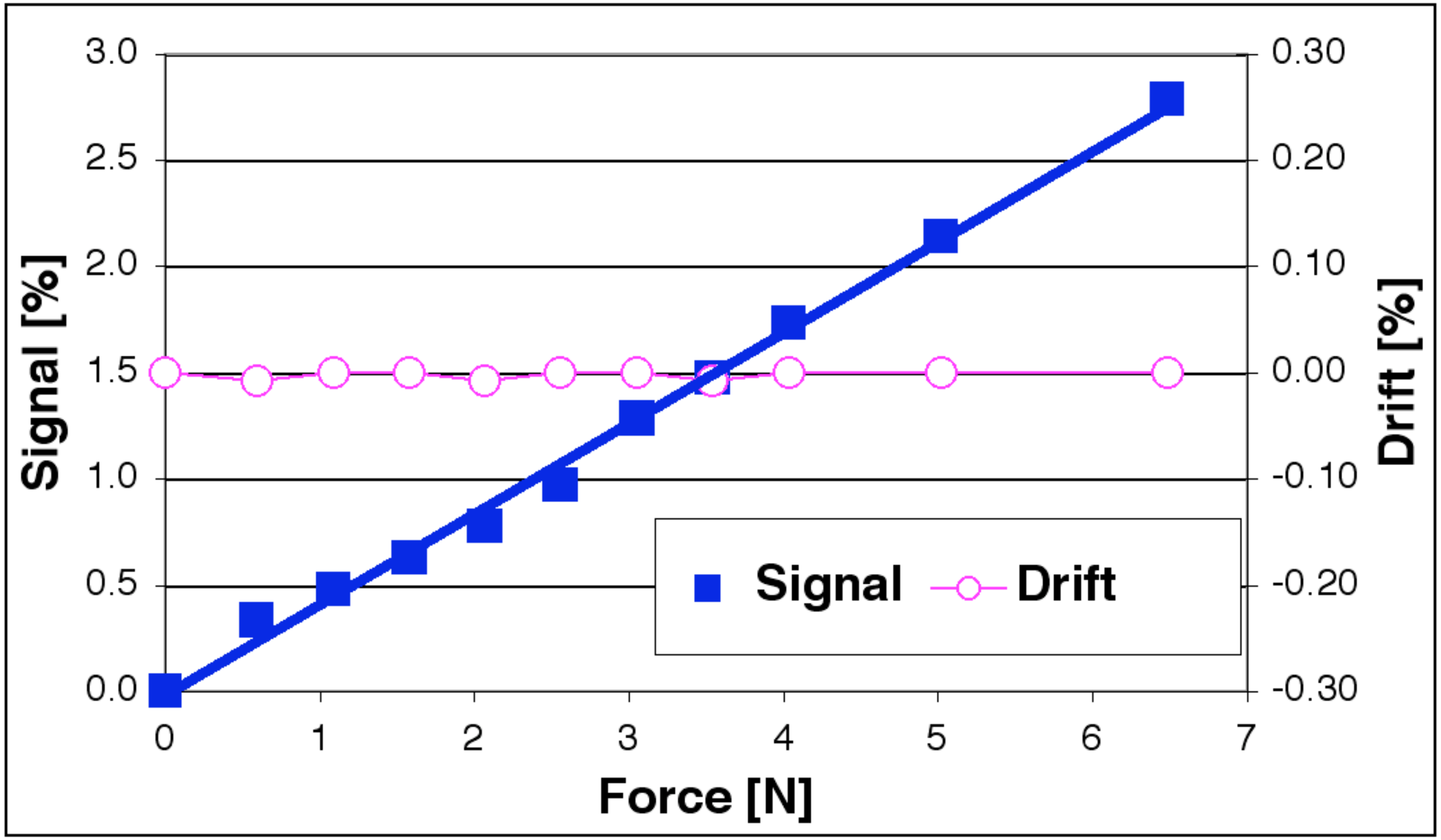


Low-temperature conductor on glass-TiO_2 dielectric

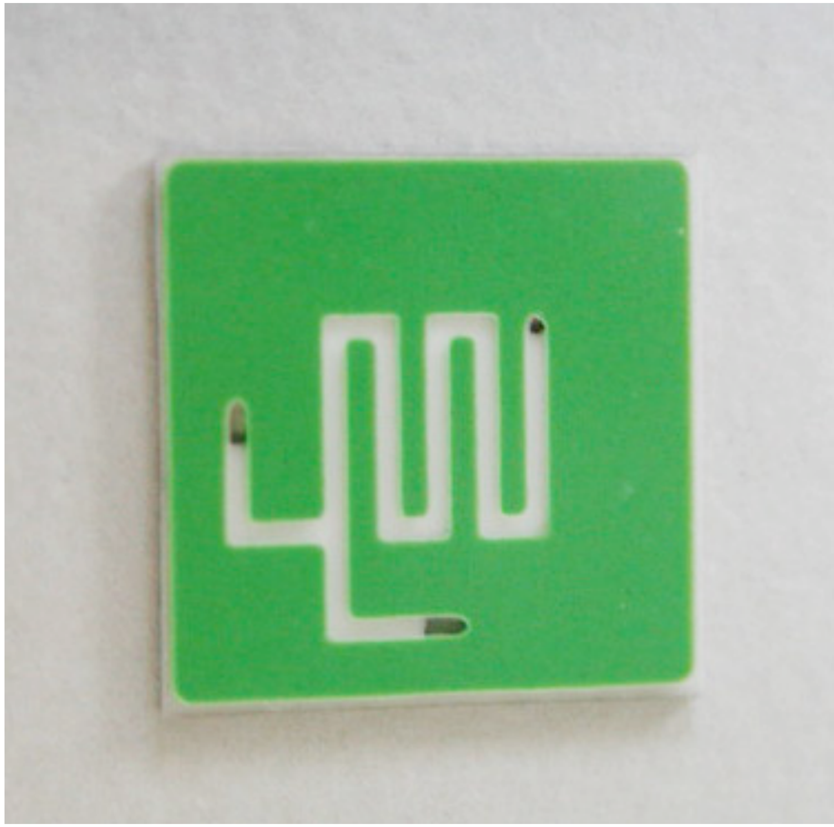
Application: prototype load cell on Al

Single resistor fired onto Al beam at 575°C

Application: prototype load cell on Al



Application: glass sealing of microreactor



- Alumina or glass module bonded to glass plate
- Channel walls: thick-film dielectric
- Seal: glass thick-film
- Improvement of chemical resistance and refire stability by using reactive TiO_2 filler in dielectric & seal

Conclusions

- Low-temperature (firing at 500…600°C) thick-film system needed for applications on glass, steel, Al and Ti alloys
- Low-temperature resistors studied
  - Understanding of piezotransport properties
  - Achieved good piezoresistors (GF≈15) below 600°C
- First low-temperature dielectrics: glass stabilised by Al_2O_3, SiO_2 or TiO_2
- Temperature compatibility achieved with glass, steel, Ti and some Al alloys
- Demonstrator force sensor on Al!

Outlook

- **Resistors**
  - Now trying 500°C - minimum in lead borosilicate system
  - Understanding of TCR, glass composition & additives
  - Understanding of (in)stability - temperature & voltage
- **Low-temperature dielectrics**
  - Combining stabilisation & expansion matching
  - Understanding & achieving chemical compatibilty with resistors
- **Processing**: controlling debinding at low temperatures
- **Materials**: other materials than Pb-based glass (toxic) & RuO_2 (expensive)?