Low-temperature thick-film piezoresistors: from solid-state physics to industrial applications

Claudio Grimaldi	EPFL-Lausanne
Thomas Maeder	EPFL-Lausanne & Sensile Technologies
Sonia Vionnet-Menot	EPFL-Lausanne
Caroline Jacq	EPFL-Lausanne
Hansu Birol	EPFL-Lausanne
Peter Ryser	EPFL-Lausanne
Sigfrid Strässler	EPFL-Lausanne & Sensile Technologies

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Summary

- Overview of thick-film resistors (TFRs) as piezoresistors
- Applications of TFRs in pressure or force sensors - benefits of a low-temperature system
- Effects of firing temperature and metal concentration on the (piezo)transport properties of low-temperature TFRs
- Stabilisation of low-temperature dielectrics
- Demonstrator
- Conclusions & outlook

Thick-film resistors (TFRs): overview of preparation

TFRs are made from random dispersions of insulating and conducting particles

Insulating phase: $PbO:B_2O_3:SiO_2$ (most common), $PbO:SiO_2:Al_2O_3$, $SiO_2:Na_2O:CaO$

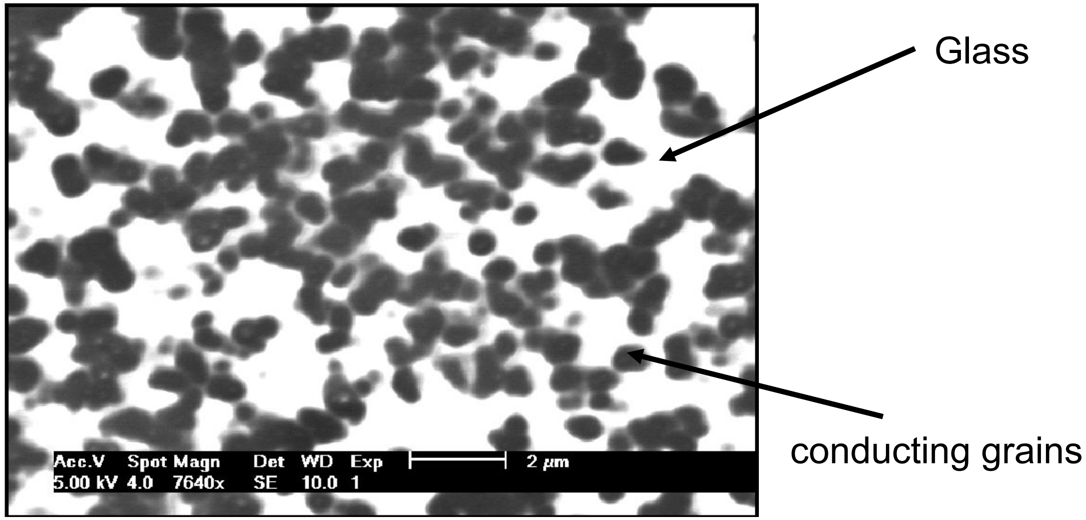
Conducting phase: RuO_2 (most common), $Pb_2Ru_2O_{6.5}$, $Bi_2Ru_2O_7$

also IrO_2, $BaPbO_3$, $Pb_3Rh_7O_{15}$

An organic vehicle is added and the pastes are screen printed on alumina substrates

Thermal treatment is made at firing temperatures T_f higher than the glass softening temperature

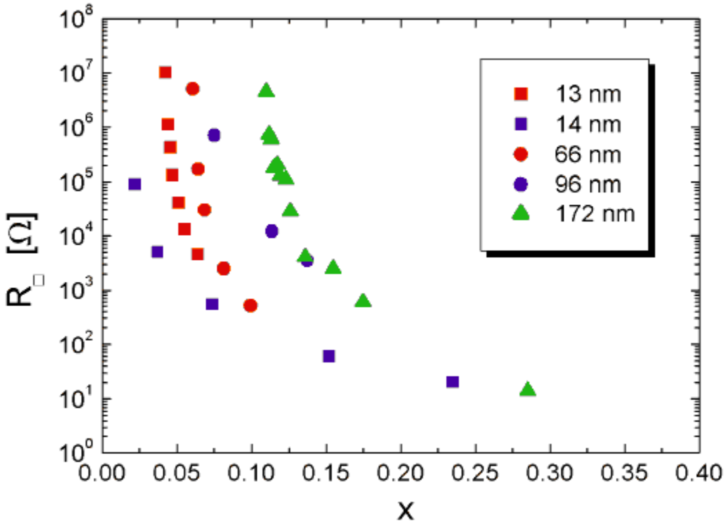
The final TFR is dense and compact



Thick-film resistors (TFRs): overview of transport properties

V_M = total volume of conducting particles V_G = total volume of insulating grains

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



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

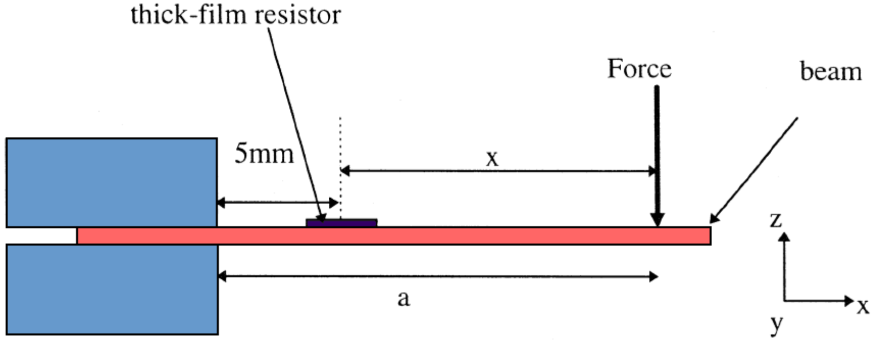
$$R \cong R_0(x-x_c)^{-t}$$

which indicates <u>percolative behavior</u>

Thick-film resistors (TFRs): overview of 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

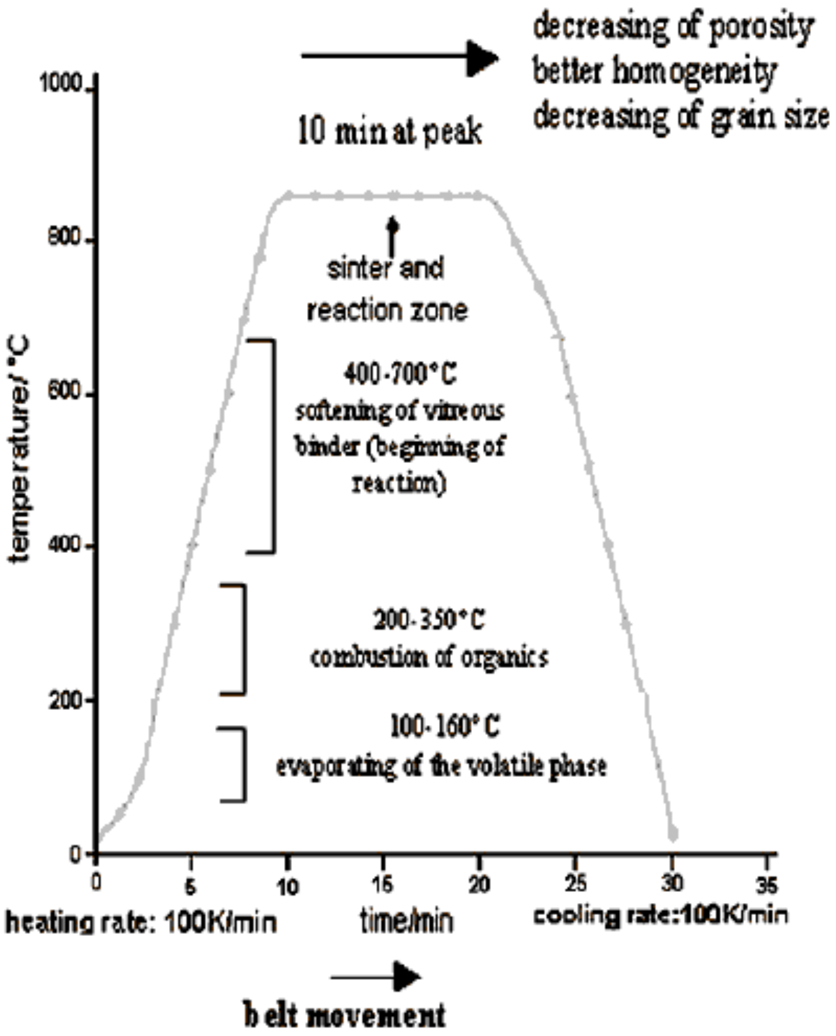
$$K = \frac{\Delta R}{\varepsilon R} = \frac{\Delta \rho}{\varepsilon \rho} + \text{geometric contribution}$$

The piezoresistive factor

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

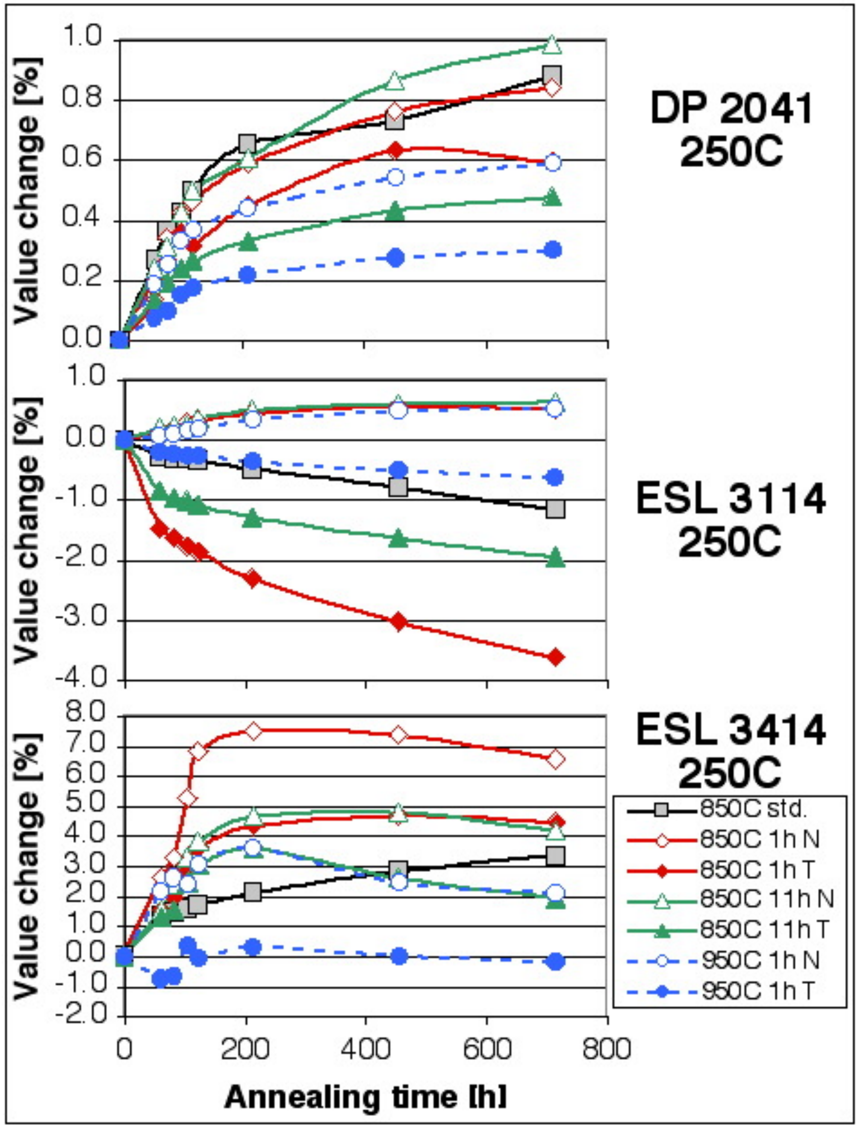
can be as high as $\Gamma \approx 30$

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

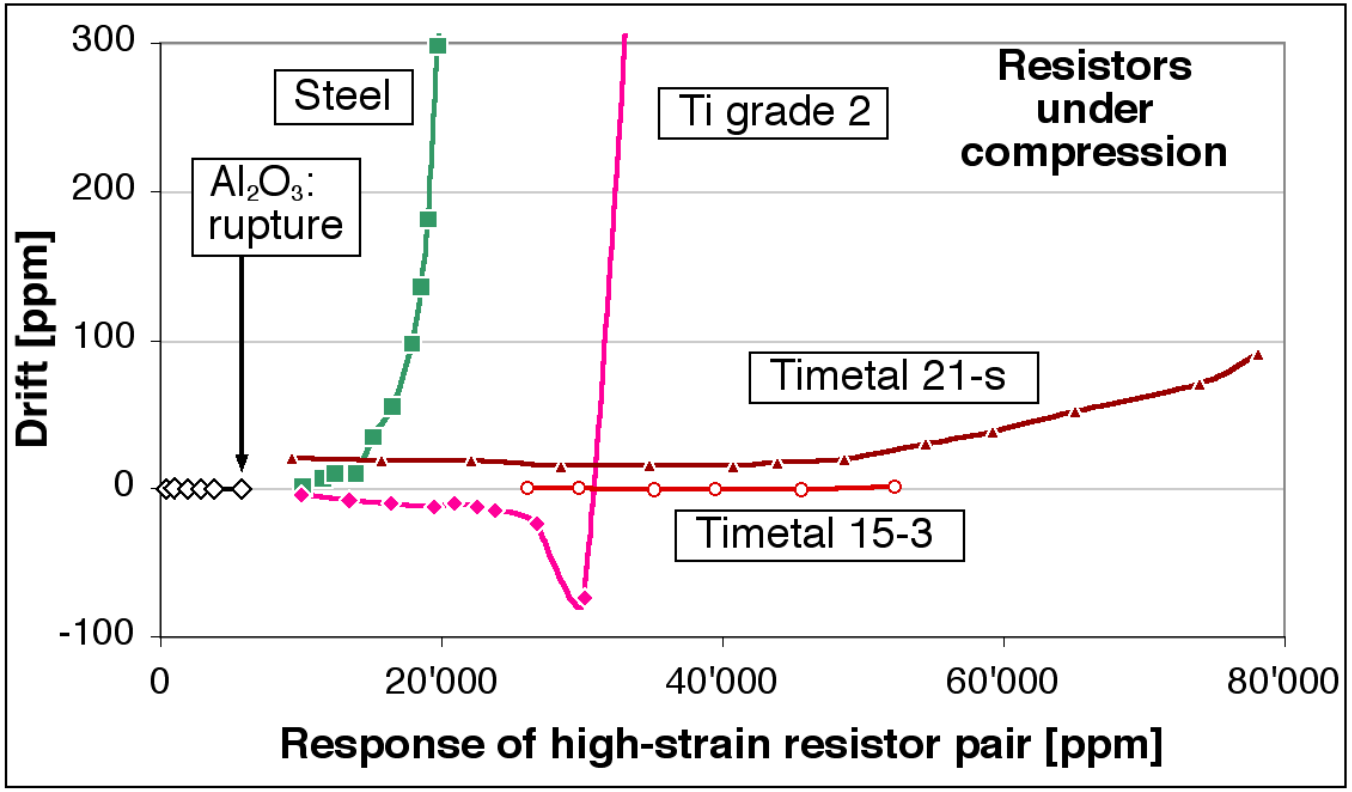
Thick-film resistors (TFRs): stability



Vionnet & al., 2004

- 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

Thick-film resistors (TFRs): high piezoresistive response



Jacq & al., 2004

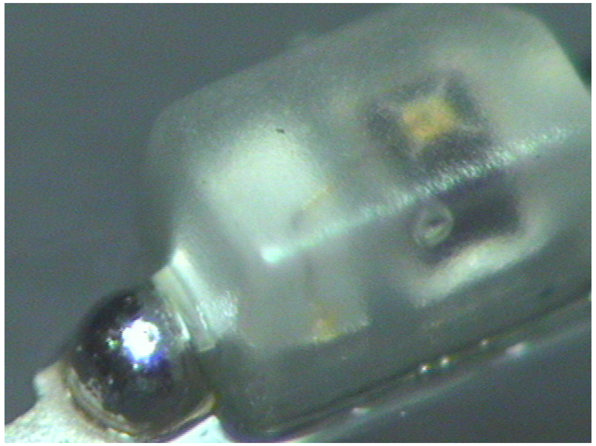
- Ultra high response possible: > 5%!
- Not practical: rapid oxidation of Ti & Ti alloys above 600°C - **need ≤ 600°C system!**

Applications: low-temperature thick-film (piezo)resistors

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

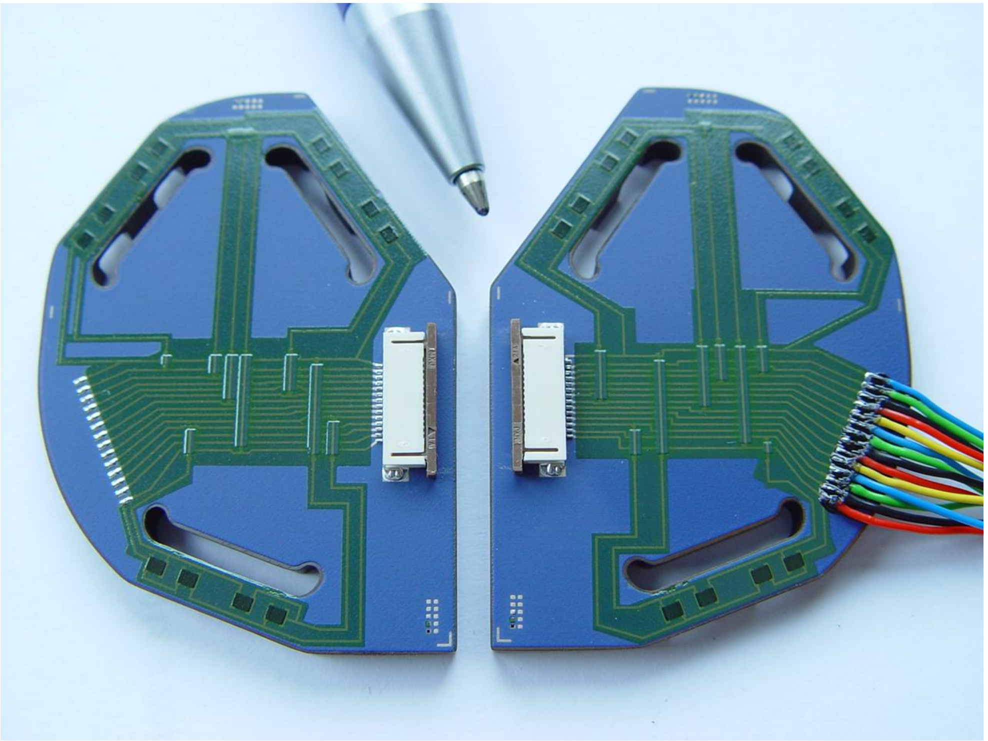
* Commercially available

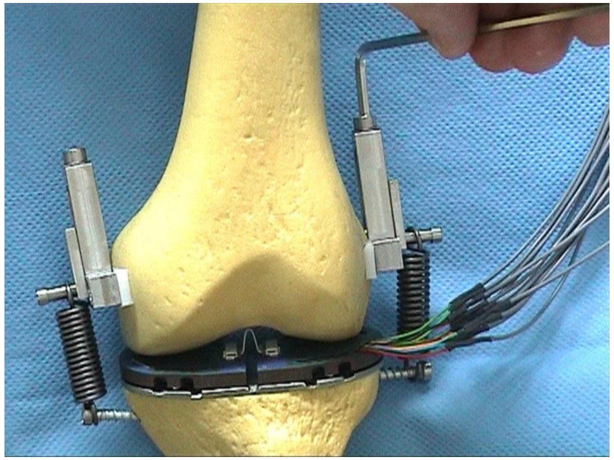
Thick-film pressure sensor on steel, Huba Control DT 510

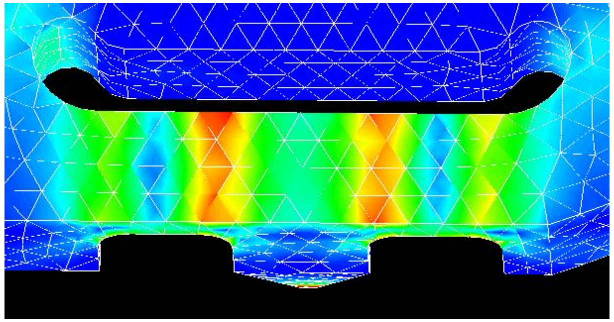


LED on glass thick-film circuit

Applications: a knee force sensor







- 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

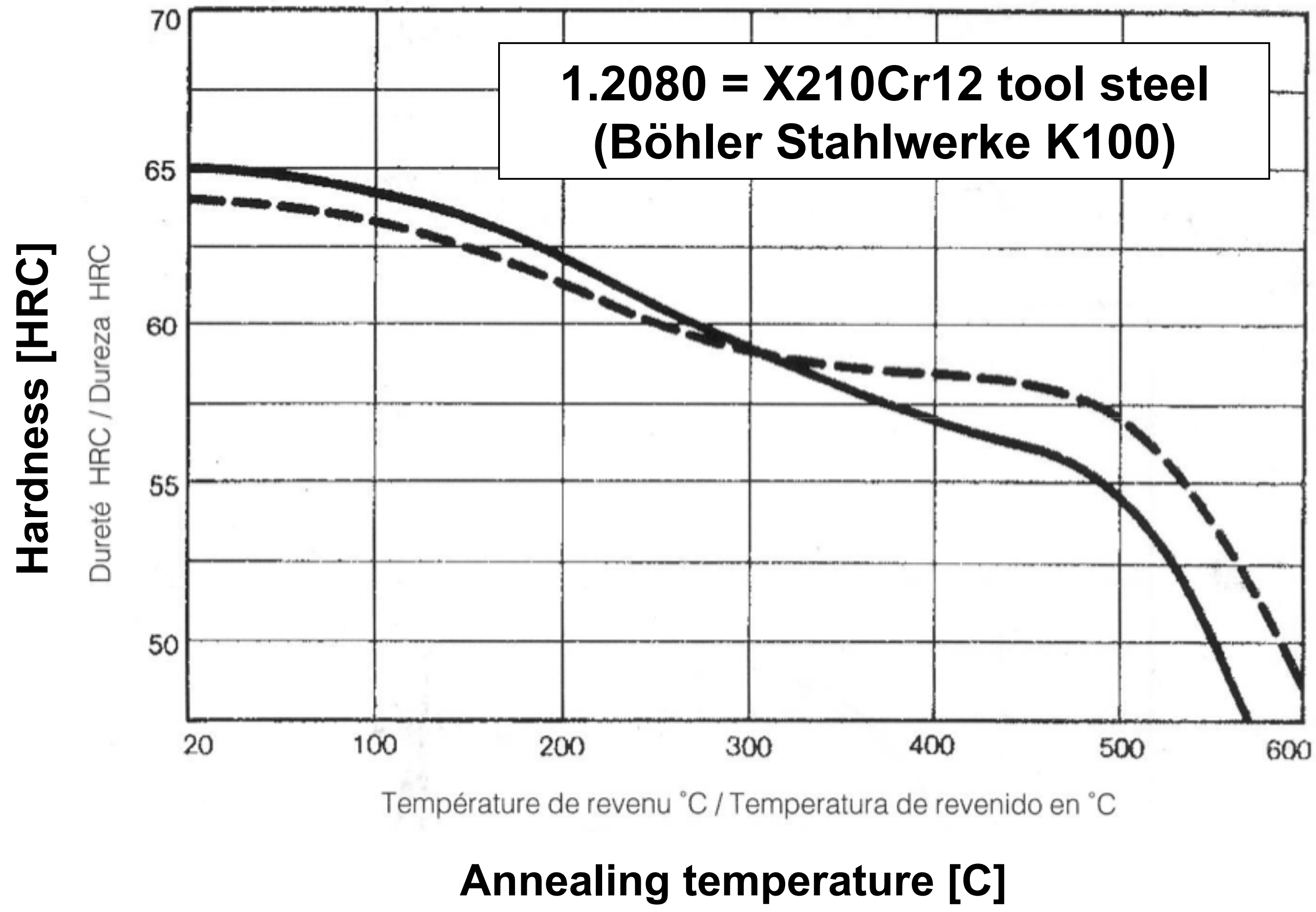
- **Oxidation** - most stainless steels have sufficient oxidation resistance for the standard thick-film process.

- **Adherence of dielectric** - many commercial dielectric compositions available - Co as adhesion promoter.

- **Softening** - the effect of cold work and/or heat treatment are essentially lost!

- **Martensitic transformation** - disruptive volume change => cracking of dielectric!

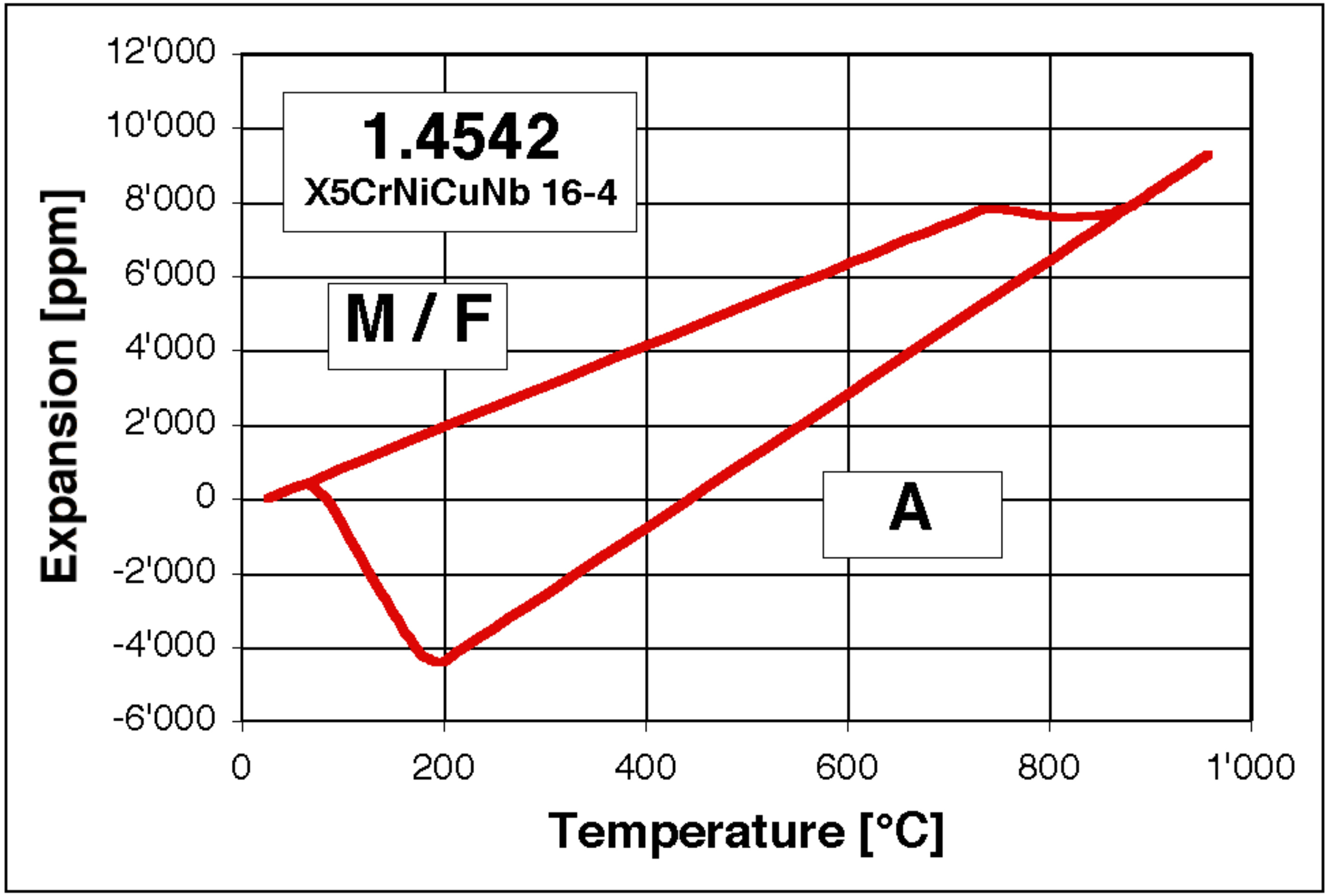
Steel - softening at high temperature



1.2080 = X210Cr12 tool steel
(Böhler Stahlwerke K100)

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

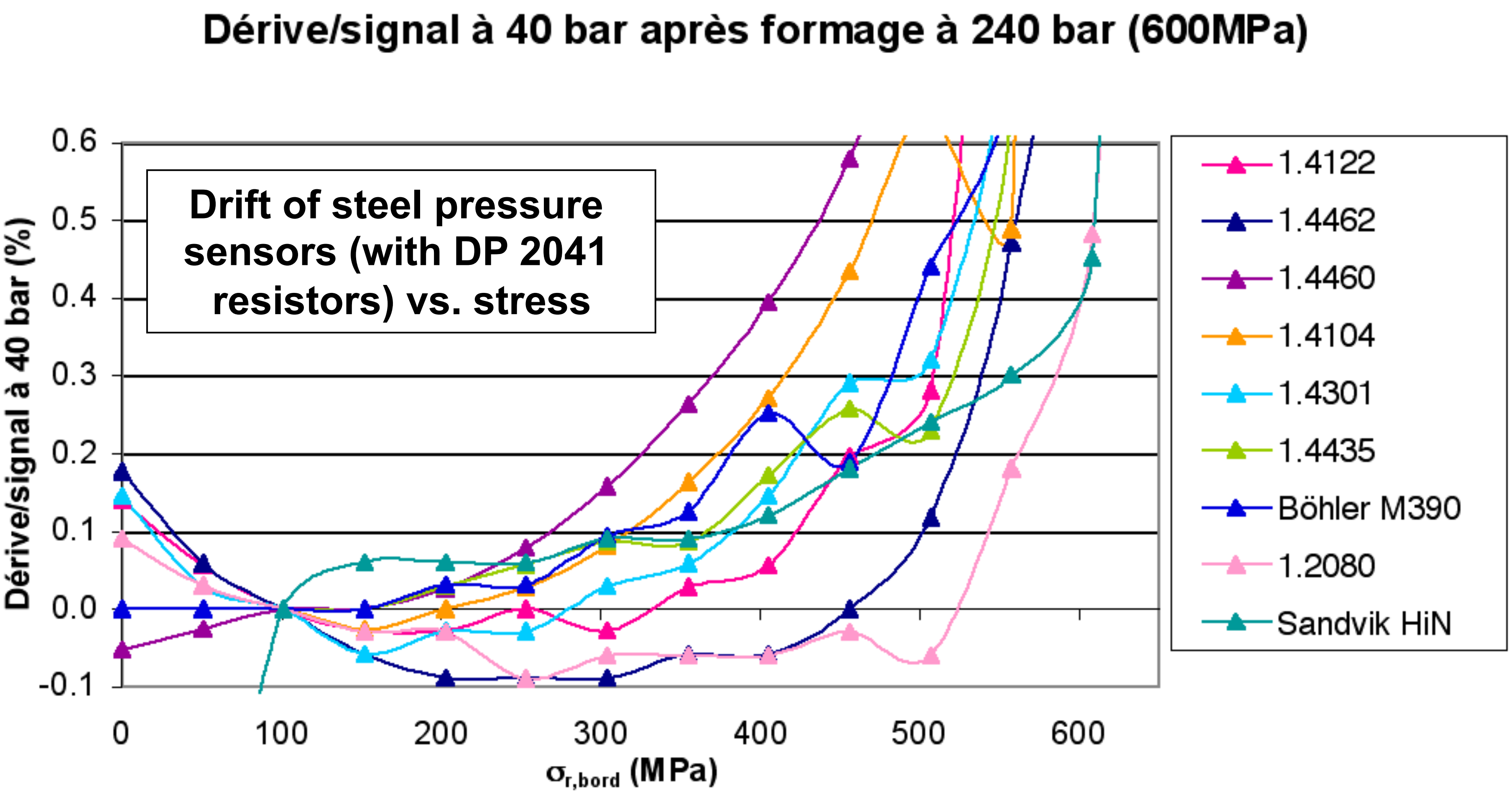
Steel - martensitic transformation



- Must avoid disruptive martensitic transformation!
- Work below 700°C!

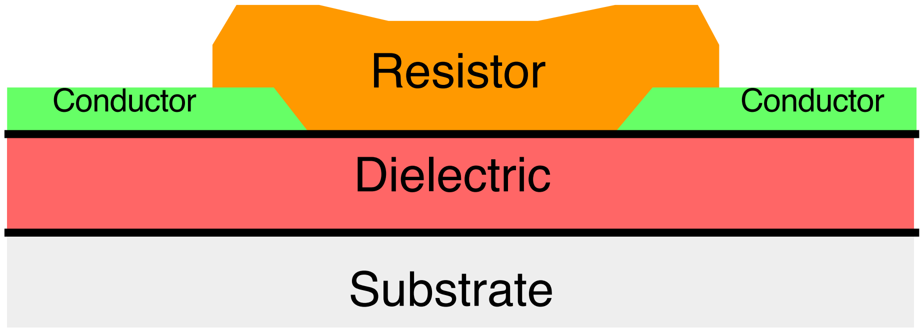
Vionnet & Maeder 2000

Steel - current thick-film pressure sensors



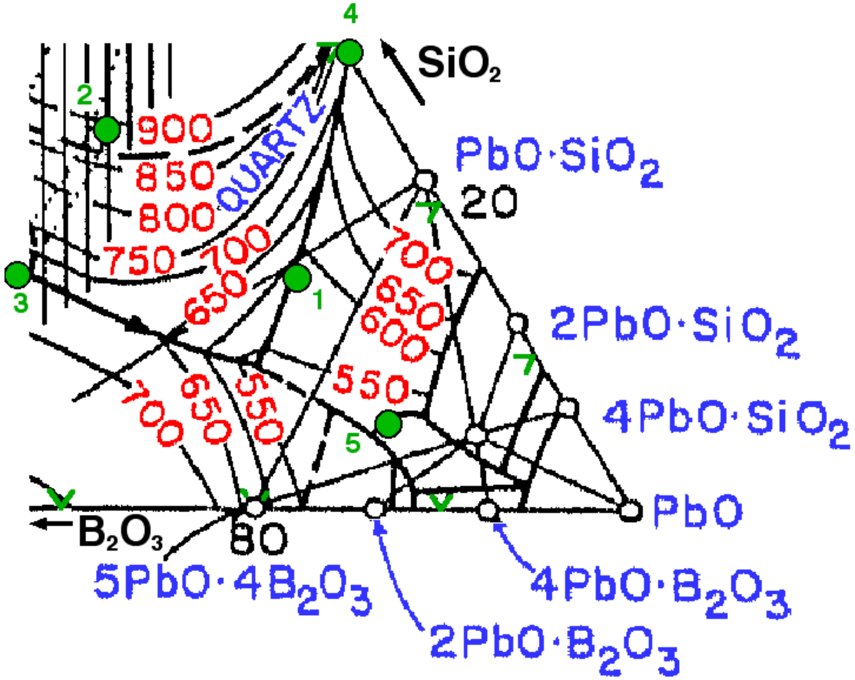
- ☐ Sufficient for rugged low-precision sensors
- ☐ High precision not possible due to softening

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

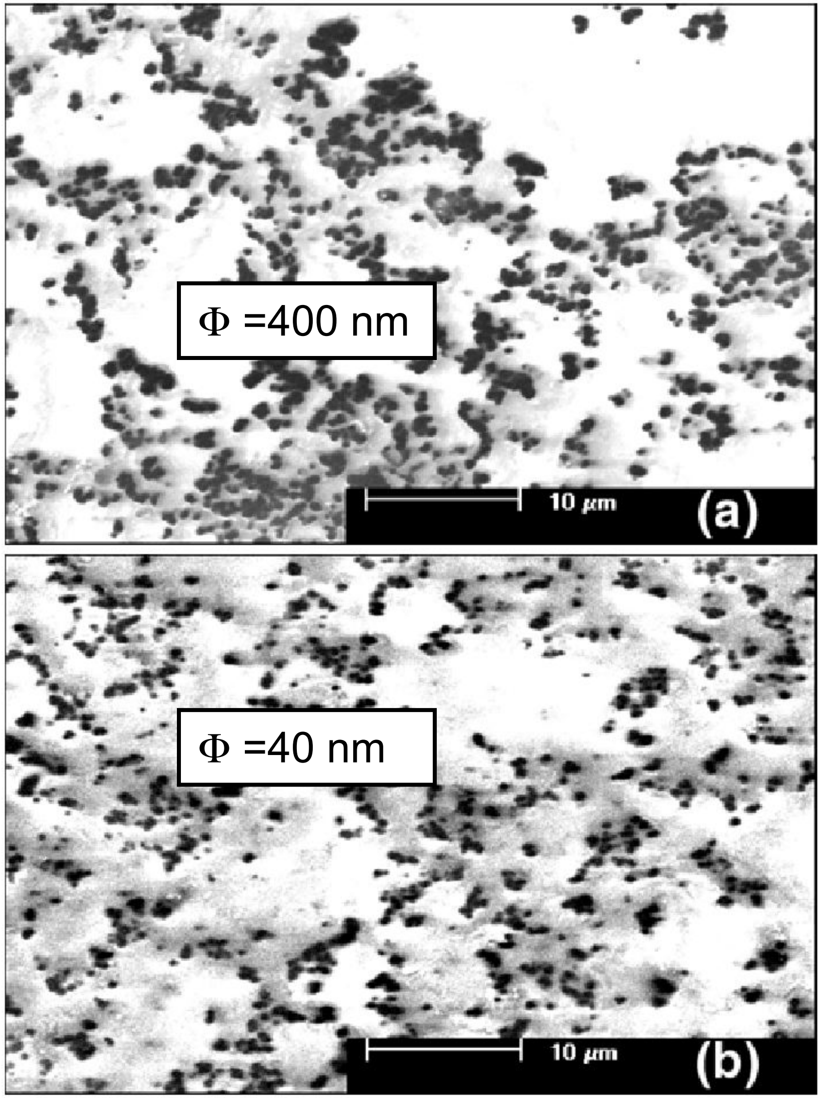


2-5% Al_2O_3 added to inhibit crystallisation

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!)

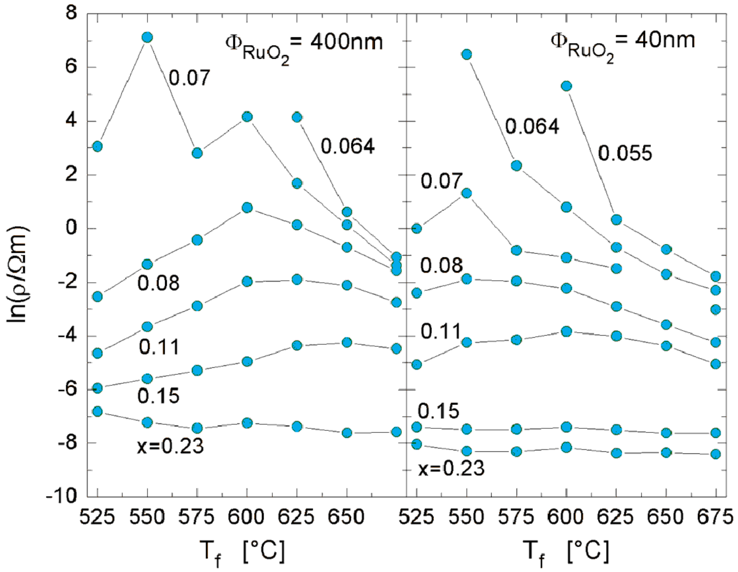
Preparation of RuO_2-based low-temperature TFRs

- 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**

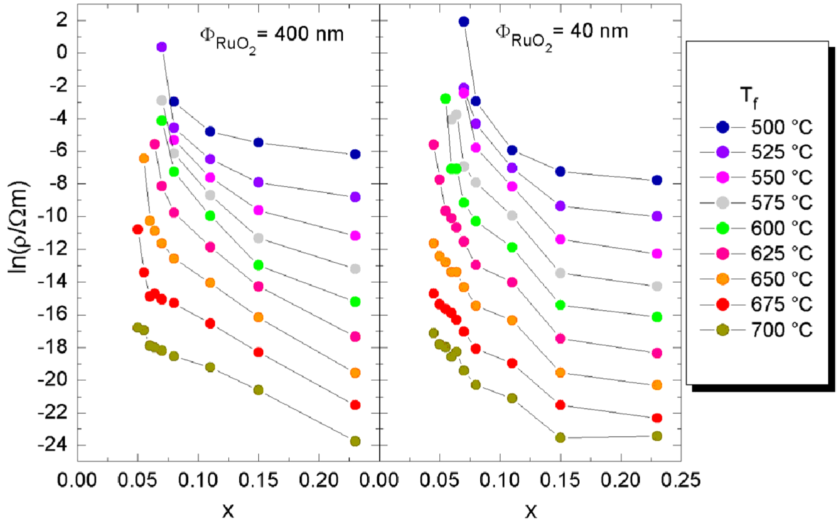


Effects of firing temperature T_f

The firing temperature T_f has important effects on TFRs transport properties

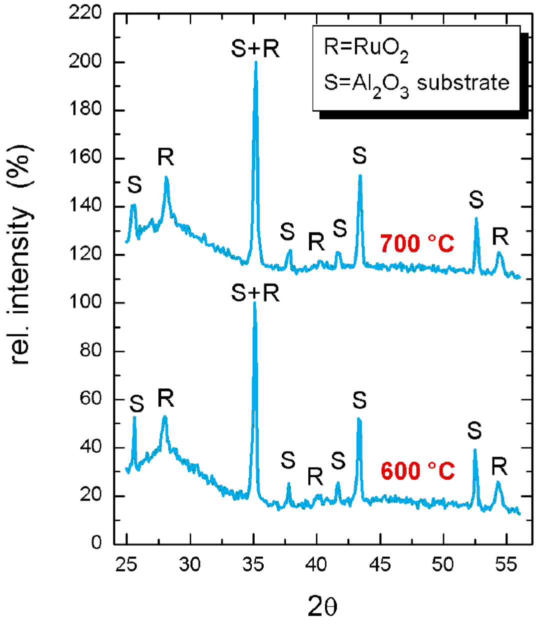


- At moderate RuO_2 concentration x the resistivity displays a maximum
- at low x the resistivity is monotonous
- at very high T_f the resistivity is weak x dependent



- 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

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

Intermediate T_f

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

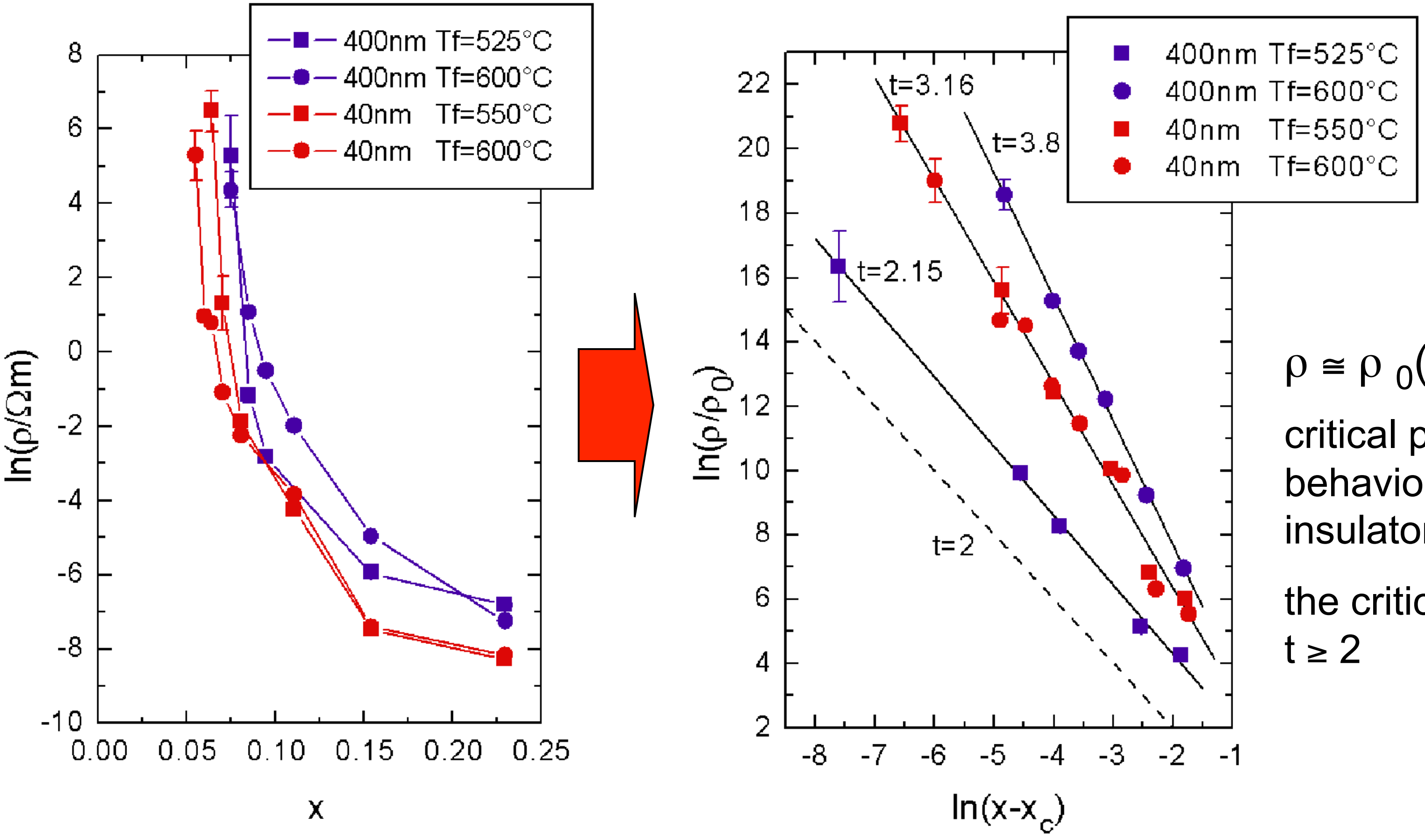
High T_f

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



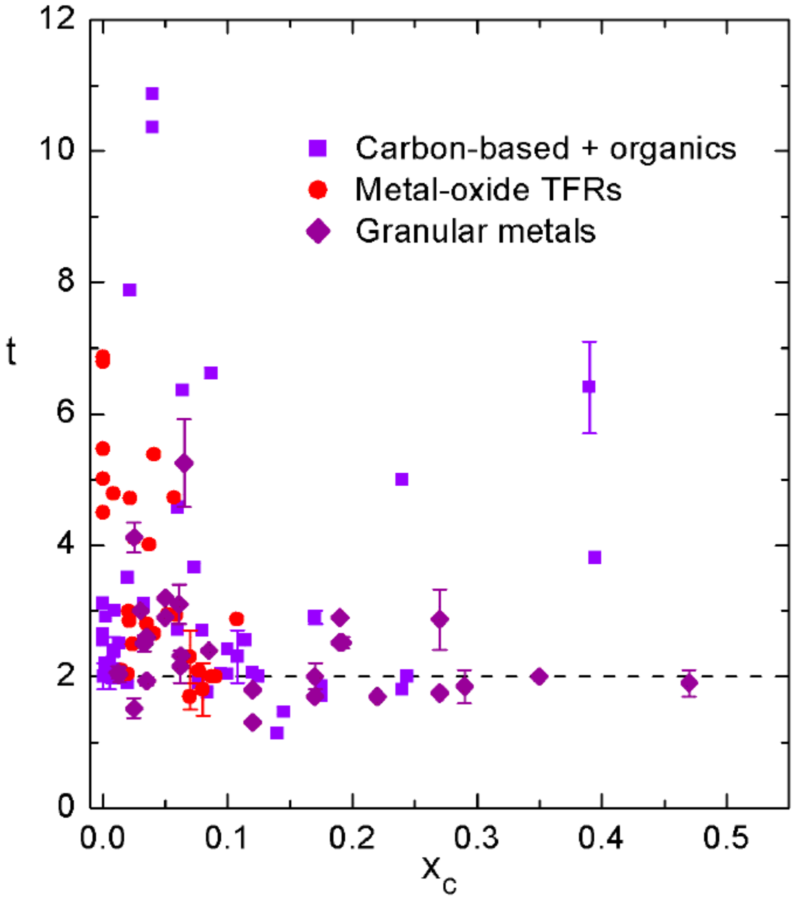
$\rho \cong \rho_0 (x-x_c)^{-t}$

critical percolative behavior close to the insulator transition

the critical exponent is $t \geq 2$

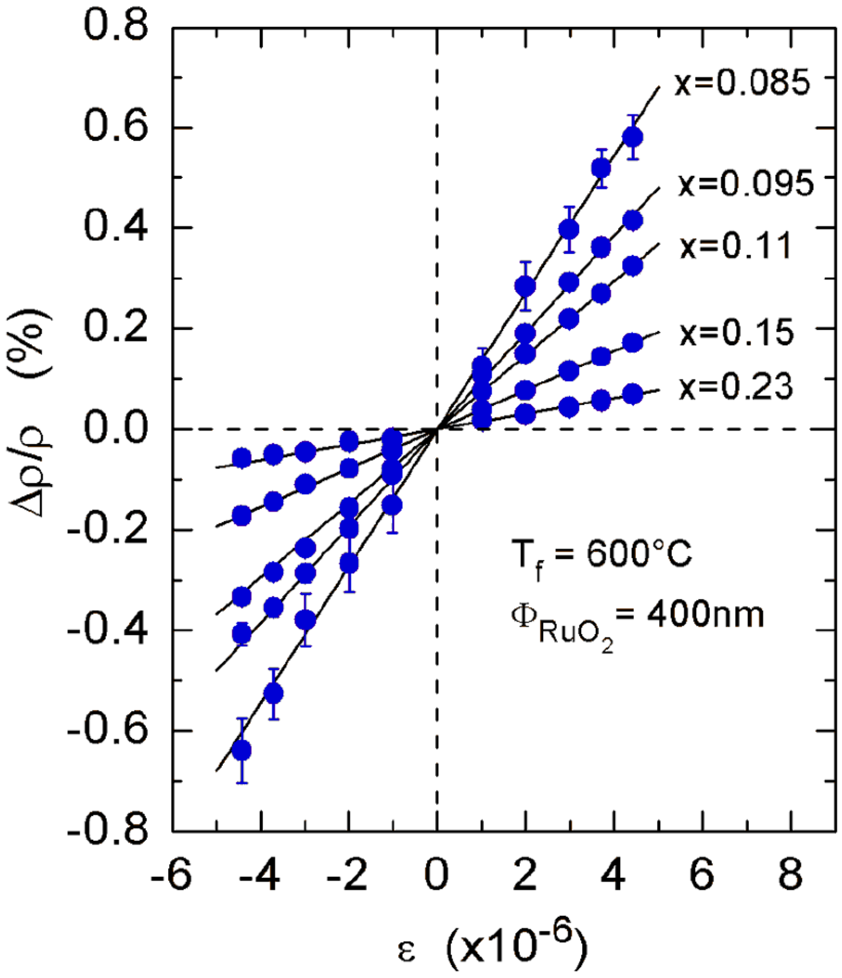
Percolation properties

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



- 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

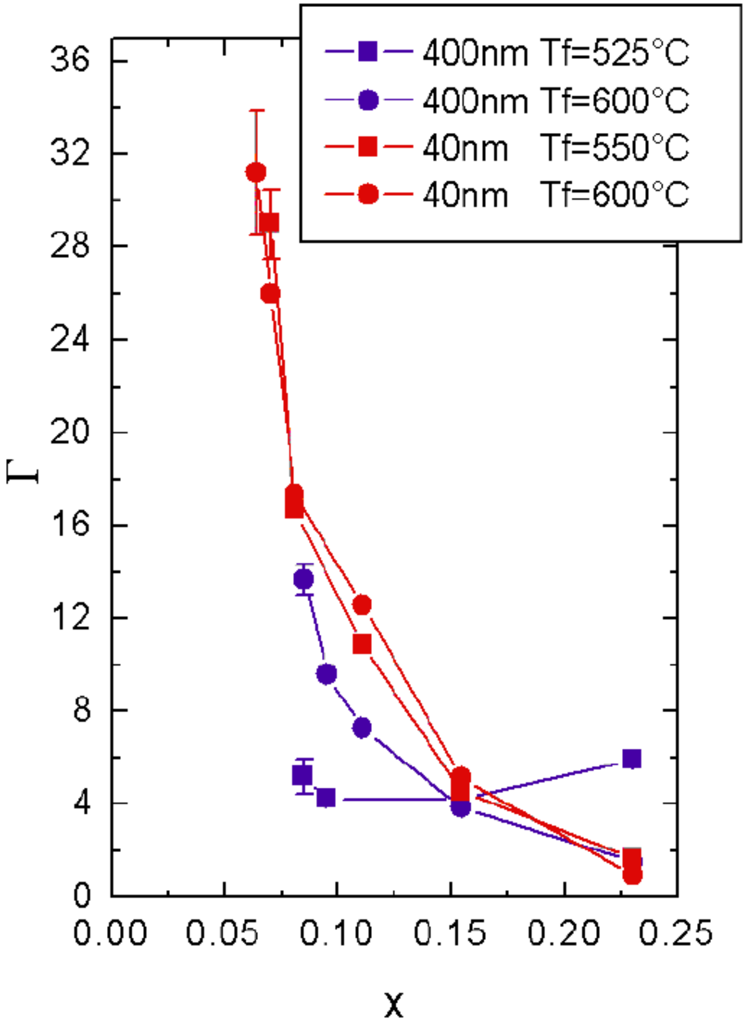


- The effect of strain is **linear and symmetric**
- there is no evidence of false signals due to possible cracks or other strain faults
- as the RuO_2 concentration x lowers, the resistivity change $\Delta\rho/\rho$ increases
- the piezoresistive factor

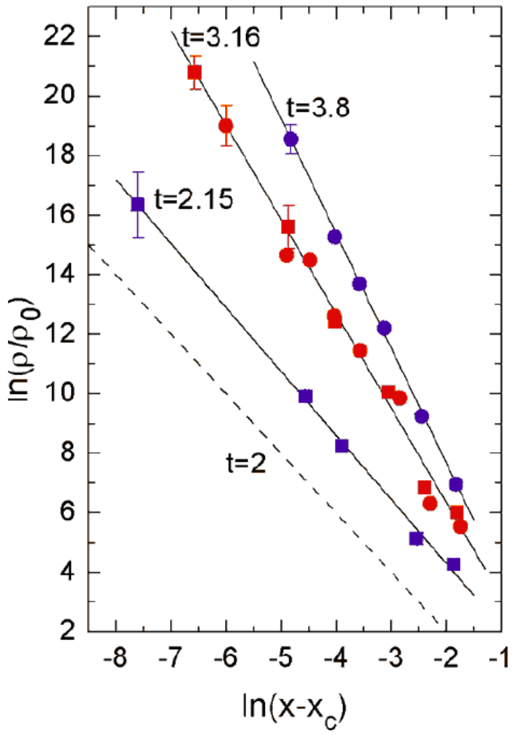
$$\Gamma = d \ln(\rho)/d\varepsilon$$

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 $\rho \rightarrow \infty$

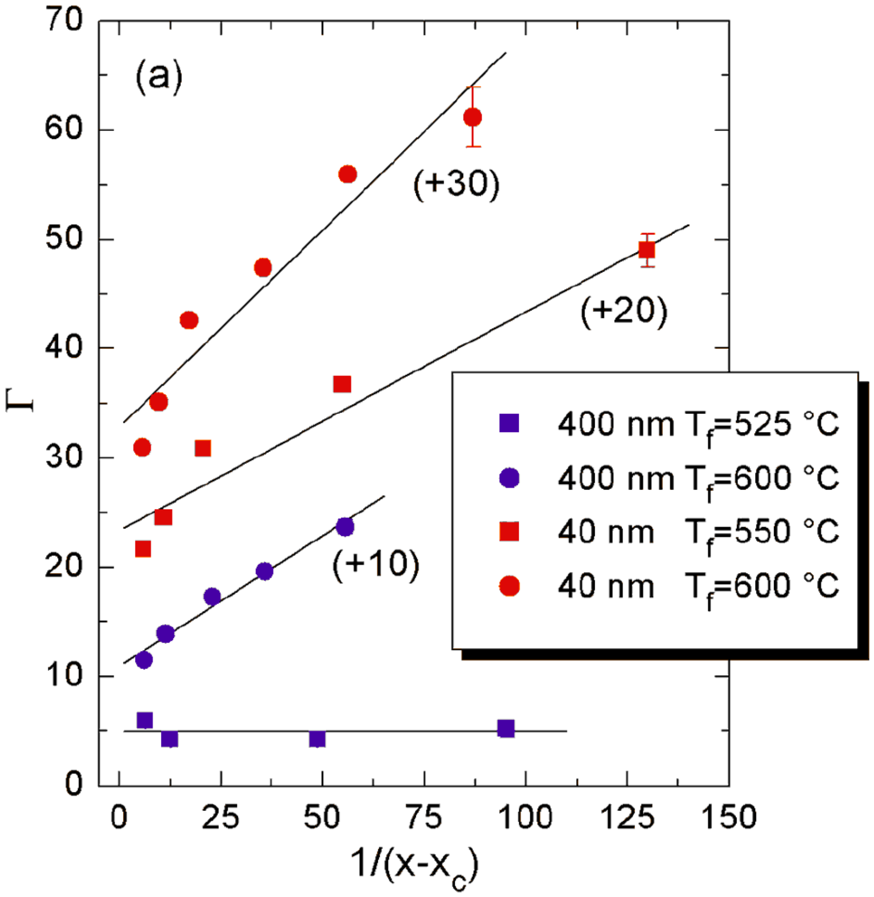


It appears that there is a **correlation** between diverging Γ and non-universal behavior of transport (t>2)

Effect of percolation on piezoresistive properties

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

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

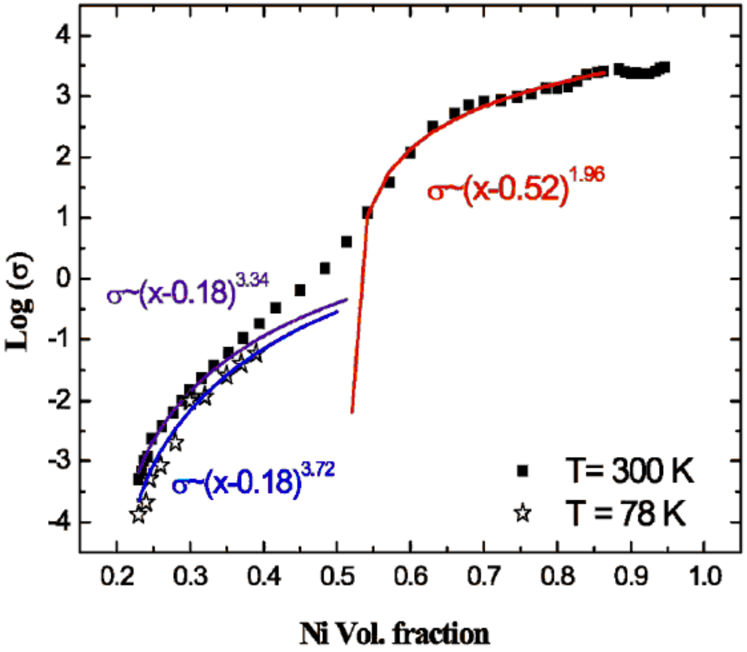


- The fits to the 40 nm series are bad
- It is not clear why the 400 nm T_f=525 °C series should not diverge
- x is just a measure of the inter-grain junctions, if $dx/d\varepsilon \neq 0$ then an applied strain would break the junctions… but the variation of resistivity is linear in ε
- A different 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**

$t = 2$ if $\upsilon + 2a/\xi < 2$

$t = \upsilon + 2a/\xi$ if if $\upsilon + 2a/\xi > 2$

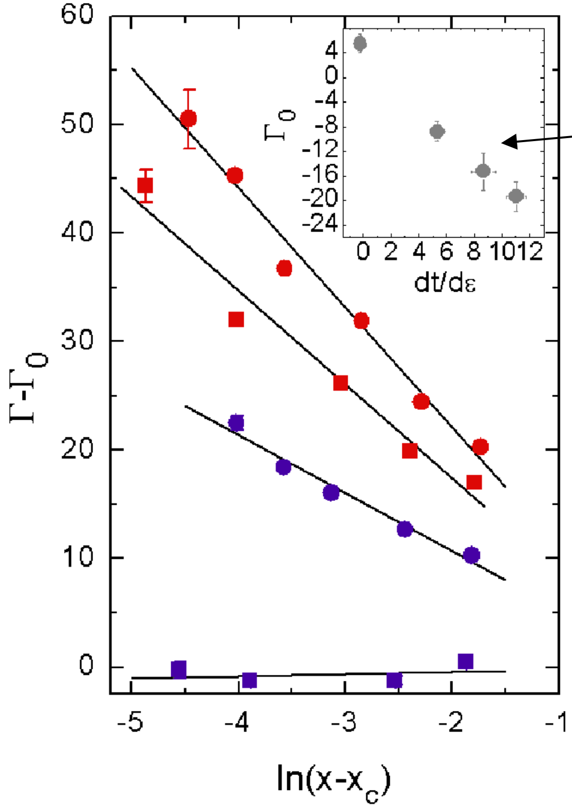
I. Balberg, Phys. Rev. Lett. **59**, 1305 (1987)

where $\upsilon = 0.88$ is the correlation length exponent (a geometrical quantity)

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

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

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



$\Gamma_0 \propto -dt/d\varepsilon$

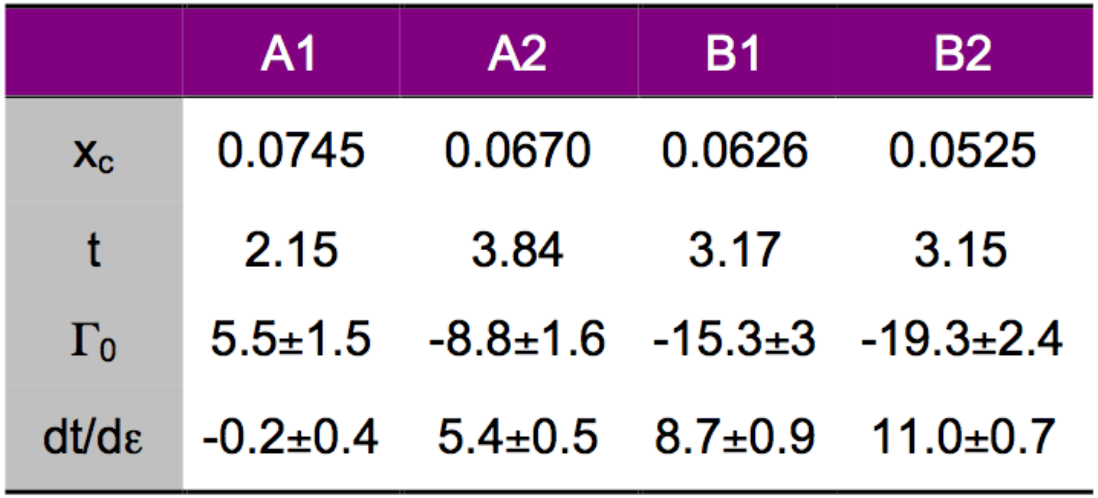
Effect of percolation on piezoresistive properties

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
$dt/d\varepsilon$	-0.2±0.4	5.4±0.5	8.7±0.9	11.0±0.7

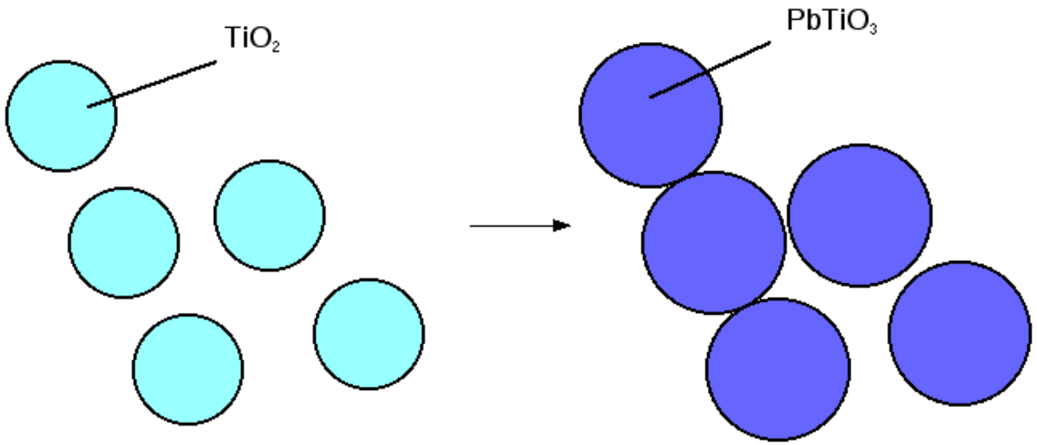
- The tunneling-percolation theory explains why when t> 2 the piezoresistivity diverges at x_c
- the logarithmic divergence fits well with the experimental data
- Monte Carlo calculations confirm that $\Gamma_0 \propto -dt/d\varepsilon$

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

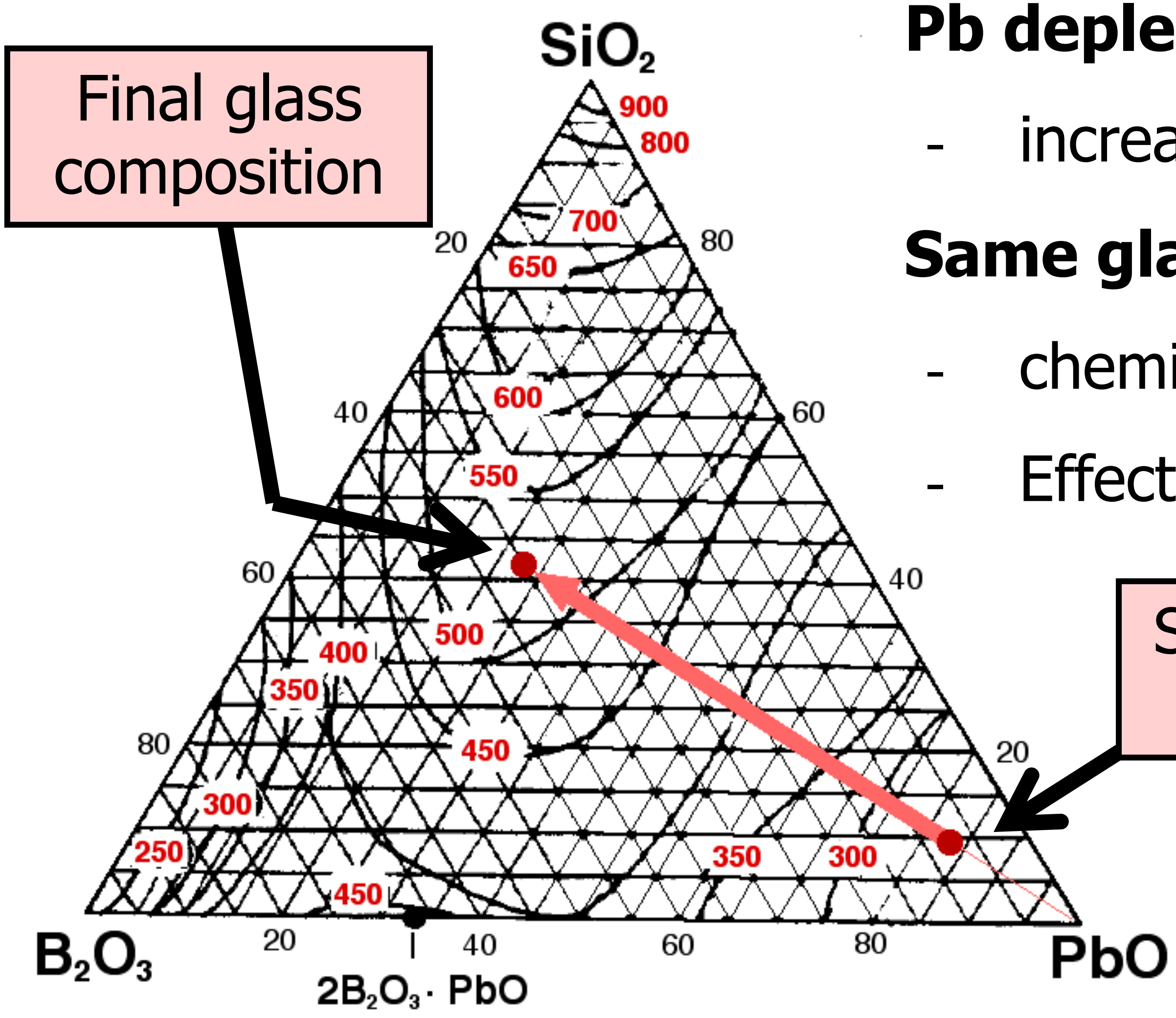


PbO (glass) + TiO_2 (nano grains) $\rightarrow$ $PbTiO_3$

Stabilisation by:

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

Dielectrics: stabilisation by TiO_2



Final glass composition

Starting glass composition

Pb depletion

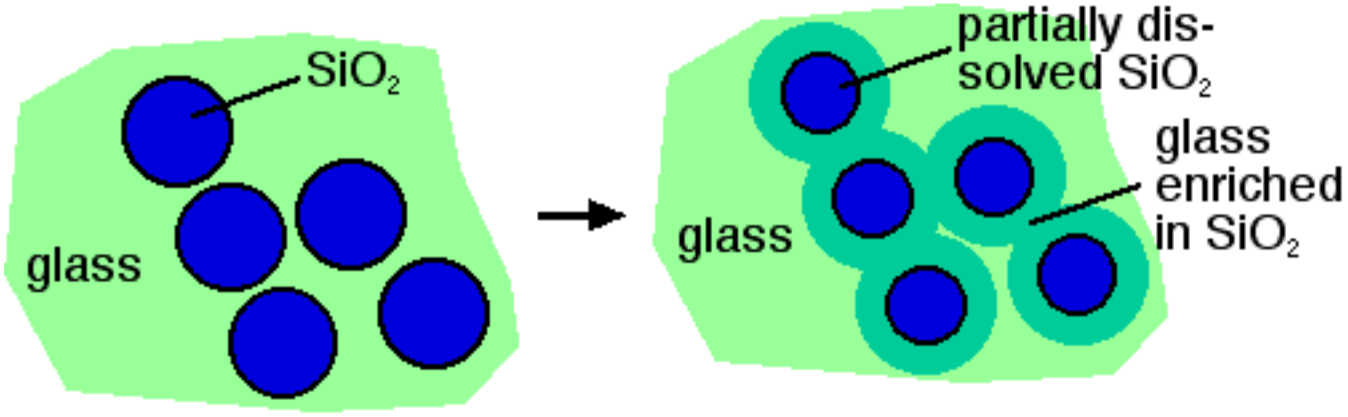
- increase of melting point

Same glass as resistors

- chemical compatibility
- Effect of TiO_2?

Dielectrics: stabilisation by SiO_2

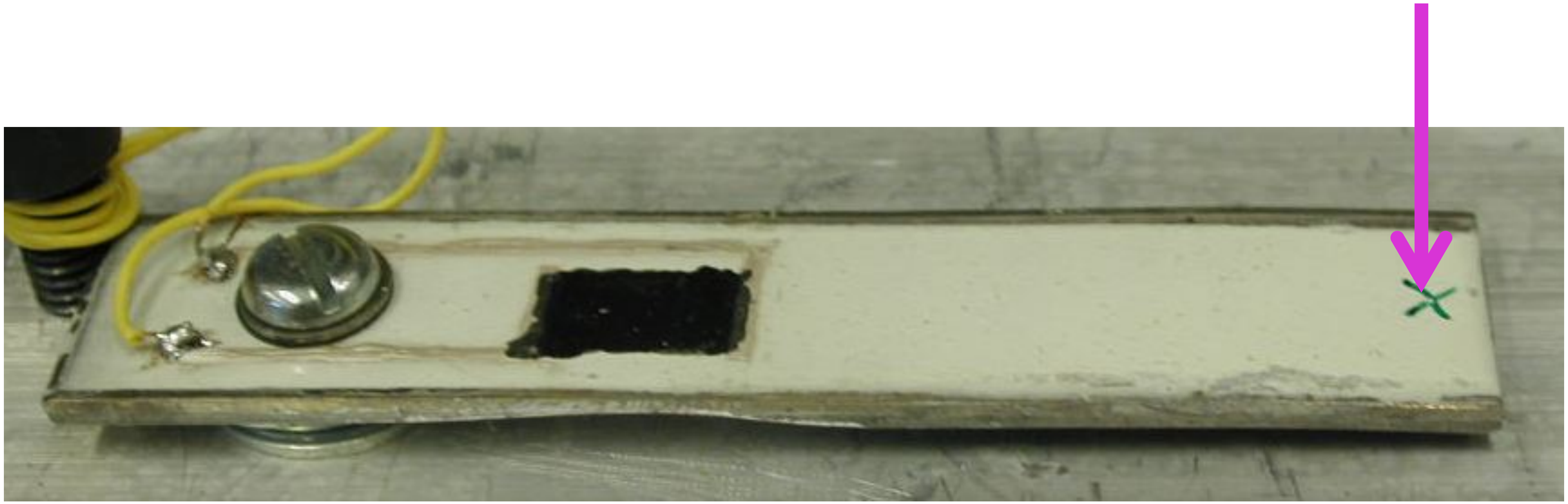
SiO_2
particles &
low-temp.
glass



glass + SiO_2 → SiO_2 - rich glass

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

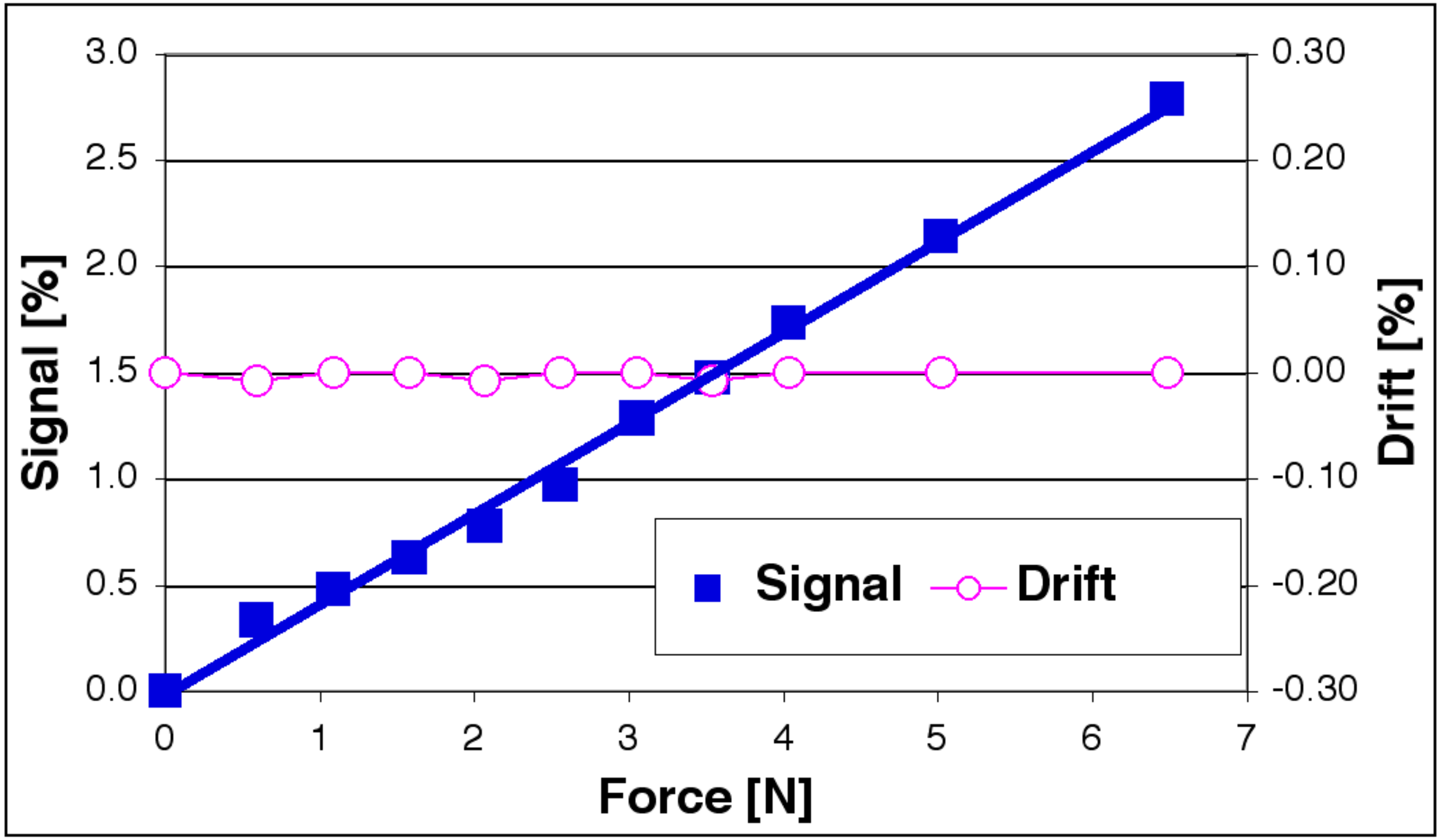
Application: prototype load cell on Al



Force

Single resistor fired onto Al beam at 575°C

Application: prototype load cell on Al



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 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)?