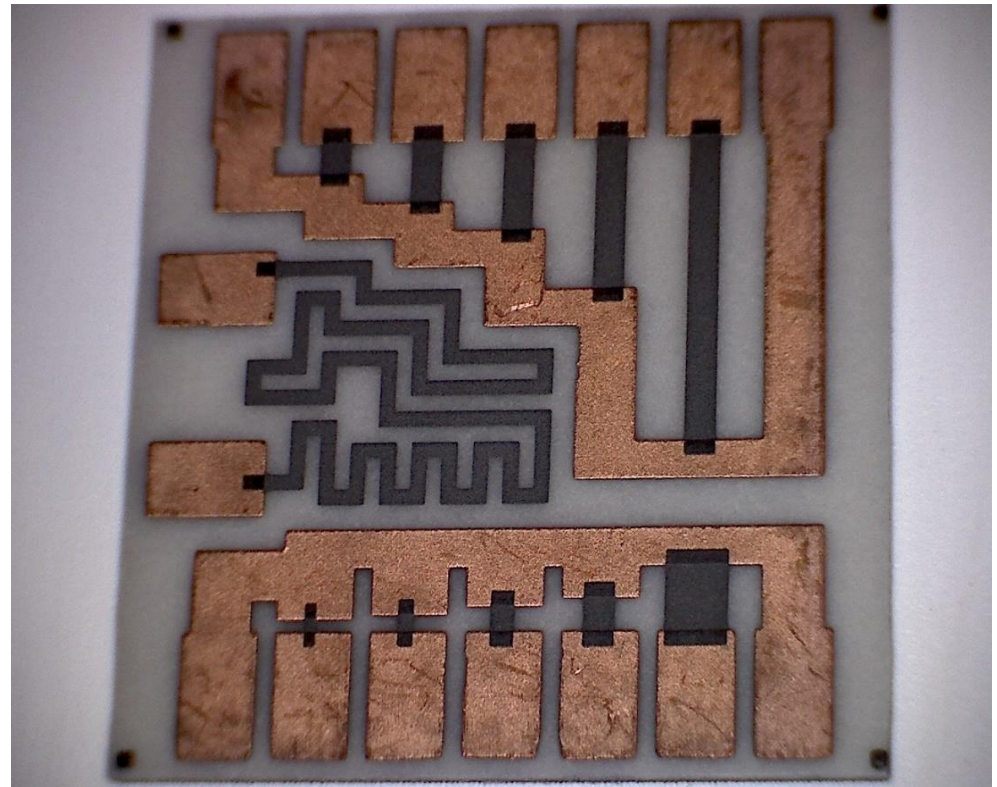


***Ruthenium-Containing Conductive Ceramics (RCCC)
for High Ohm Value Resistors on Al_2O_3 / AlN Substrates
and High Temperature Firing HTCC Structures***

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August 15th, 2015

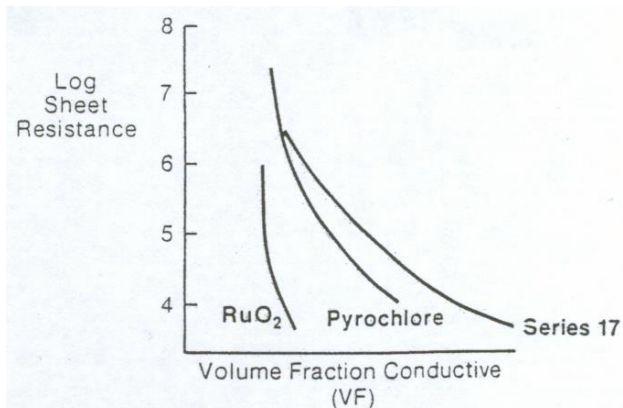


Outline

1. A Necessity in Conductive Phase Other Than RuO ₂ and Pyrochlores for High Ohm Value Resistors	2
2. Anomalous Conduction Loss Problem Solving	3
3. Ruthenium-Containing Conductive Ceramics (RCCC)	4
2. Thick Film Resistors Based on Ruthenium-Containing Conductive Ceramics	8
3. Surface Quality of Ultra High Ohm Value Thick Film Resistors Based on RCCC	9
4. Directly Fired in Nitrogen Ni/Cr/Ru Series for AlN Substrates	10
5. High Temperature Storage of High Ohm Value Resistors on Al ₂ O ₃ Substrates	11
6. Samples of High Ohm Value Resistors on AlN Substrates for High Temperature Storage ...	15
7. High Temperature Storage of High Ohm Value Resistors on AlN vs. Al ₂ O ₃ Substrates	16
8. Summary	17
9. List of Refereed Publications	19

A Necessity in Conductive Phase Other Than RuO₂ and Pyrochlores for High Ohm Value Resistors

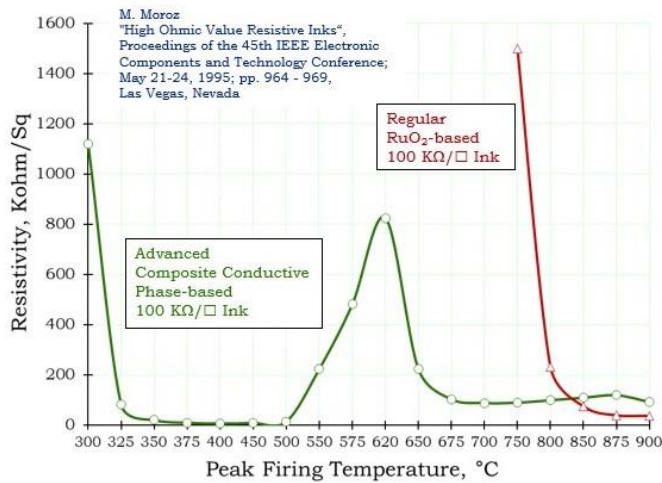
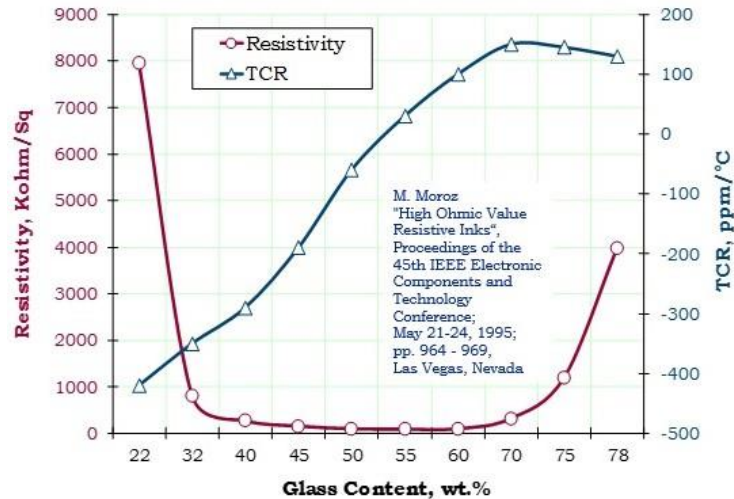
Pierce, Kutly, Larry, "The Chemistry and Stability of Ruthenium-Based Resistors", Third European Hybrid Microelectronics Conference 1981, Avignon, pp.283-301



- The properties of resistors having a low content of conductor phase relative to glass are extremely sensitive to the content of components and processing parameters
- Very small changes in content of functional phase of resistive composition alter resistor parameters to a great extent

- RuO₂ - based thick film resistors exhibit critical threshold of concentration and a critical conduction behavior
- Resistor parameters affected: sheet resistivity, TCR, sensitivity to firing conditions, and all kinds of stability
- Unacceptably steep slope of dilution curves of RuO₂ - based thick film resistors indicates **the anomalous conduction loss problem**
- The lower the slope of dilution curve, the better resistor stability is expected
- Slopes of pyrochlore-based dilution curves of commercially available resistive inks:
 - ✓ have never approached very low values
 - ✓ the only difference is how steep is the slope while it always stays quite high
- **Zero slope** of dilution curve is the **best** achievable **problem solving** result impossible for RuO₂ - based and pyrochlore-based thick film resistors at low content range of conductor phase

Anomalous Conduction Loss Problem Solving



- Screen printable ruthenium-based high ohm value resistive inks having **zero-slope of dilution curves and unique sintering ability** were developed in 1980s [1,2,3] by the author
- There were two major types of such inks:
 - 1) Fine powders of special composite conductive phases were obtained by precipitation from solutions. They were directly used in resistive paste compositions. Then ceramic-type resistor structures were formed during firing process of screen printed inks at the temperature range 900°C – 1,000°C in conveyor belt furnace
 - 2) For second type of resistive inks, fine powders of composite conductive phases were mixed with glasses and ceramic fillers like colloidal alumina. Water-based high-viscosity slurry was formed by special technique with no pressing process. After drying pre-formed whole piece of the powder composition was sintered at 900°C – 1,000°C and quenched into water for following crushing and grinding. Then ground powders were used for screen printable resistive inks of the second type

Ruthenium-Containing Conductive Ceramics (RCCC)

1

An advanced technique of RCCC manufacturing has been invented. RCCC has been used as conductive phase for screen printable high ohm value high stability resistor inks on alumina and AlN substrates:

- RTCC may be sintered from the ingredients directly during firing of screen printed resistive inks in belt furnace at 900°C – 1,000°C in the form of printed elements on the substrate
- RTCC for screen printable inks may be also pre-sintered from water-based or organic-based slurry with further grinding. The features of this process are the following:
 - ✓ no powder mix ball milling and pressing is required
 - ✓ sintering temperature may be shifted in accordance with the specific application from 900°C to 1,600°C
 - ✓ firing temperature of the resistive inks made of pre-sintered RCCC may be chosen in the temperature range from 900°C to 1,600°C

Ruthenium-Containing Conductive Ceramics (RCCC)

2

- ✓ resistive inks based on RCCC may be also fired in neutral atmosphere. A combination of this feature with firing temperature range up to 1,600°C provides a possibility for development of co-fired resistive inks for HTCC – High Temperature Co-fired Ceramics
- ✓ for achieving of wider resistivity range of resistive compositions designated for using at HTCC structures, the following methods may be used:
 - ⇒ changing the composition of RCCC, i.e.: the ratio of ruthenium-based conductive phases, glasses, and ceramic fillers
 - ⇒ addition of W and Mo powders in the composition of resistive inks for HTCC
- for some coating techniques, water- or organic-based resistive slurry with specific rheology may be applied by other methods rather than screen printing of resistive inks
 - ✓ it allows forming of much thicker or bulk ceramic-type resistors or co-fired on green HTCC tapes

Ruthenium-Containing Conductive Ceramics (RCCC)

3

- in both cases, real ceramics was formed after firing of printed ink (first type) or sintering of bulk piece (second type) at 900°C – 1,000°C because the lowest firing/sintering temperature was requested
- sintering temperature may be extended at the choice
- desired sintering temperature may be chosen in the range from 900°C up to 1,600°C by adjusting of resistive compositions
- RCCC is not necessarily to be ground for using as an ingredient of screen printable inks
- RCCC may be used for manufacturing of bulk resistors formed by employing of resistor slurry at 900°C – 1,600°C

Ruthenium-Containing Conductive Ceramics (RCCC)

4



A shatter of a whole piece of sintered at 950°C RCCC after quenching into water before following crushing and grinding

Unique technology of conductive ceramics for extremely stable thick film resistors consisting from alumina, special glasses, and ruthenium-containing conductive phase (not pure RuO_2) having unique sintering ability was developed. Calculated content of RuO_2 in the compositions was from 0.5% to 15%.

The features of this process are the following:

- ✓ suitable for sintering of conductive ceramics that obeys Ohm's law
- ✓ very little amounts of ruthenium-based compound even as low as 0.5% by weight may be extremely homogeneously distributed in the total ceramic compositions
- ✓ glasses in the composition ensure zero-porosity ceramic microstructure
- ✓ no ball milling and pressing processes are employed for preparation of homogenous slurry
- ✓ high-productivity, high-yield process
- ✓ controllable and reproducible

Thick Film Resistors Based on Ruthenium-Containing Conductive Ceramics (RCCC)

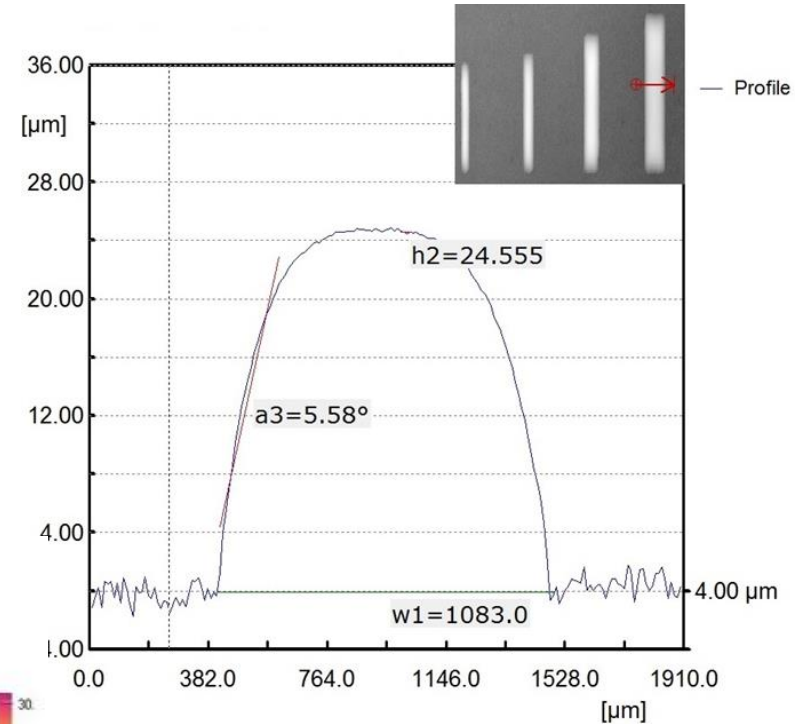
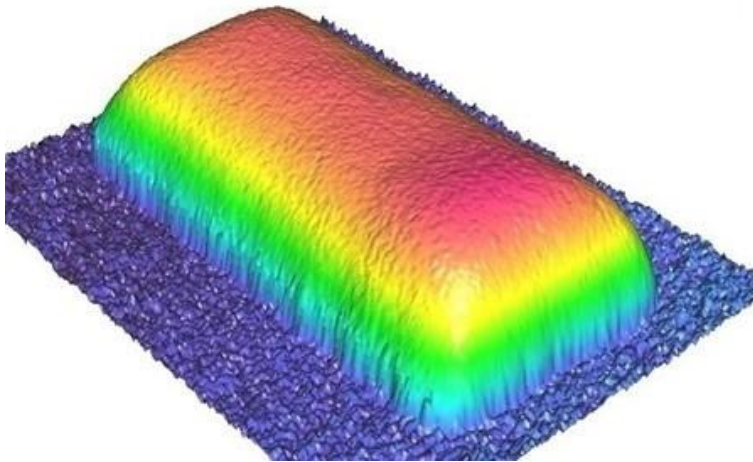
The following groups of resistive materials based on ruthenium-containing conductive ceramics (RCCC) were developed and used in production in 1980s-1990s:

- high ohm value series fired in air on alumina substrates:
 - ✓ for firing @ temperature range 900°C – 1,300°C:
 - ⇒ from 1 K Ω /□ to 1 G Ω /□
- high ohm value Ru-based series fired in air on AlN substrates:
 - ✓ for firing @ temperature range 900°C – 1,100°C:
 - ⇒ from 1 K Ω /□ to 100 M Ω /□
- directly fired in nitrogen Ni/Cr/Ru series on AlN substrates:
 - ✓ for firing @ temperature range 950°C – 1,000°C:
 - ⇒ from 20 m Ω /□ to 20 M Ω /□
- All resistive inks have fine line printing ability, at least 5-6 mil line/gap with non-sacrificed standard fired thickness

Surface Quality of Ultra High Ohm Value Thick Film Resistors Based on RCCC

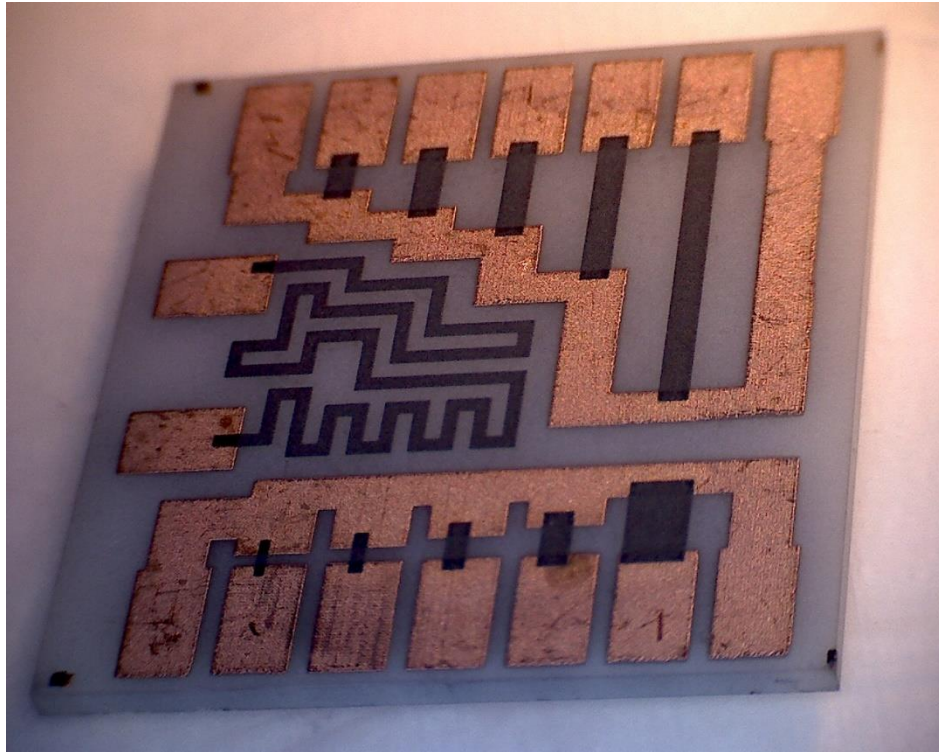


325-mesh screen, 20-mil Line/Gap
Serpentine Ultra-High Ohm Value Resistor

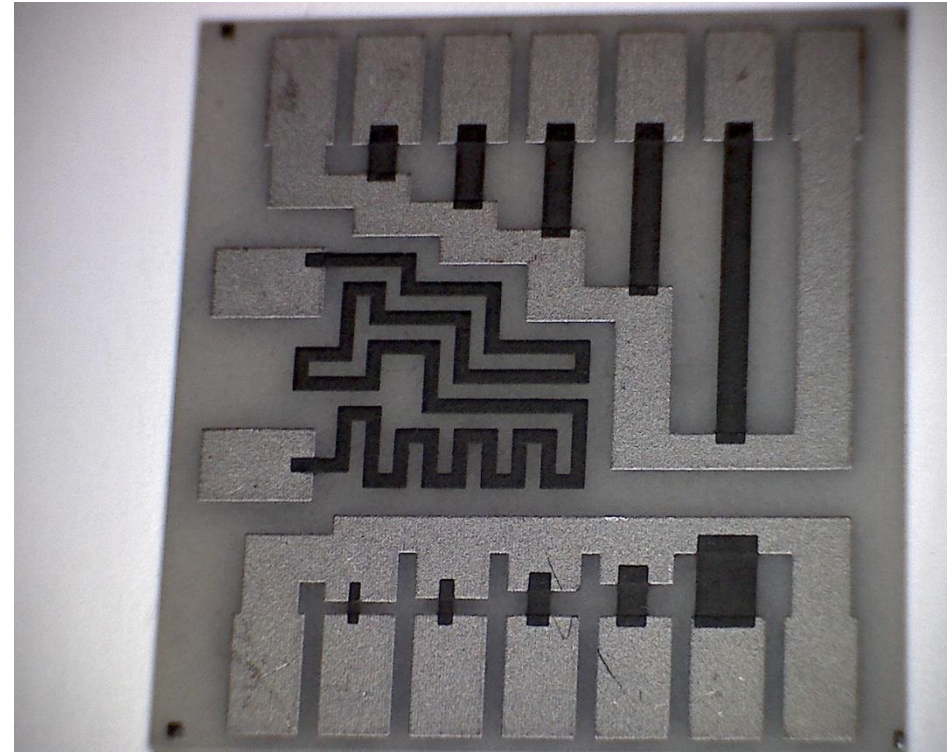


Thickness of Resistor at 145 Mesh Screen
80x80 mil Ultra-High Ohm Value Resistor

Directly Fired in Nitrogen Ni/Cr/Ru Series for AlN Substrates



8 M Ω / \square Ni/Cr/Ru resistors on AlN
900°C N₂ on Cu conductor

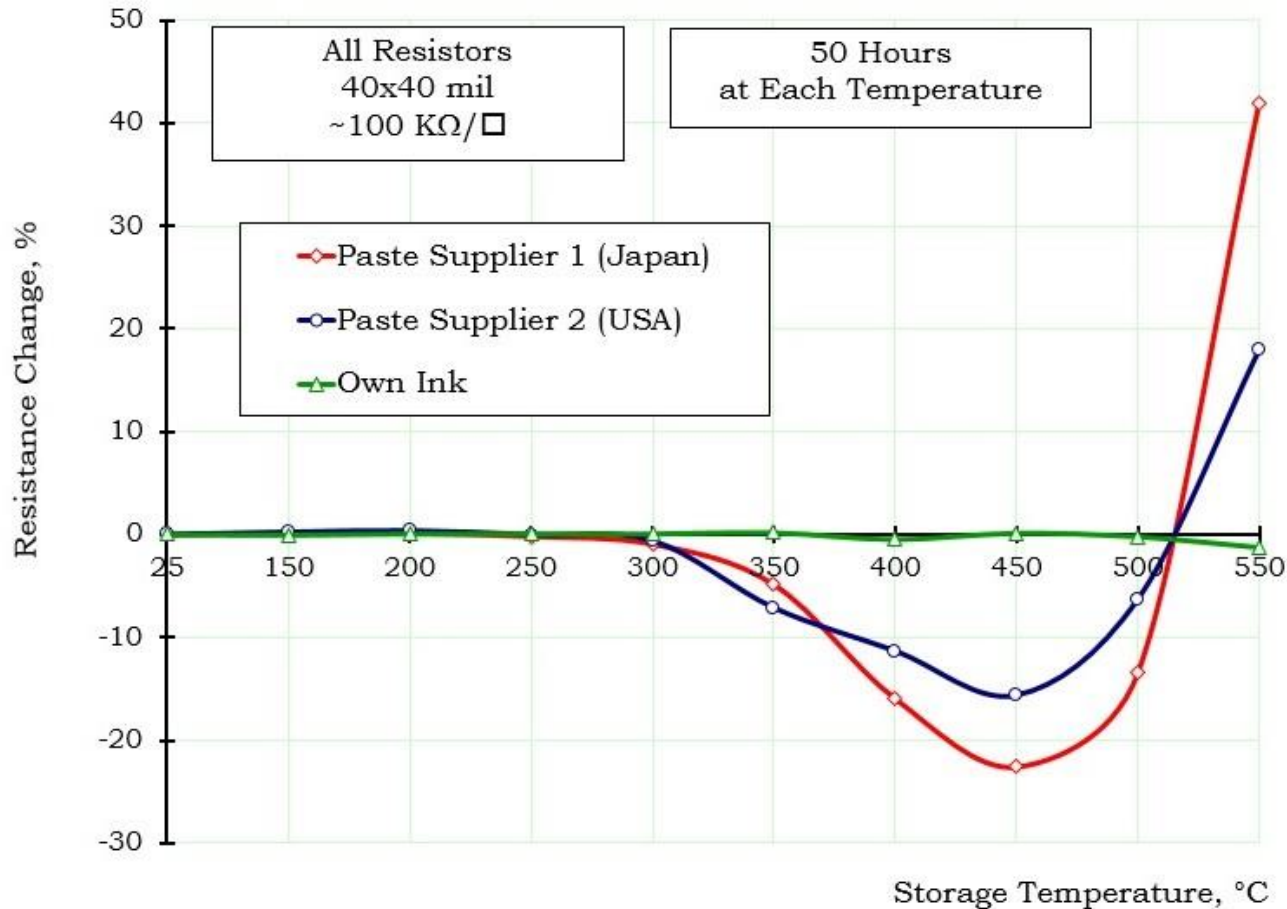


8 M Ω / \square Ni/Cr/Ru resistors on AlN
900°C N₂ on Cu/Ni conductor

Compatible Cu/Ni conductor is suitable for high temperature applications when pure copper is susceptible to oxidation

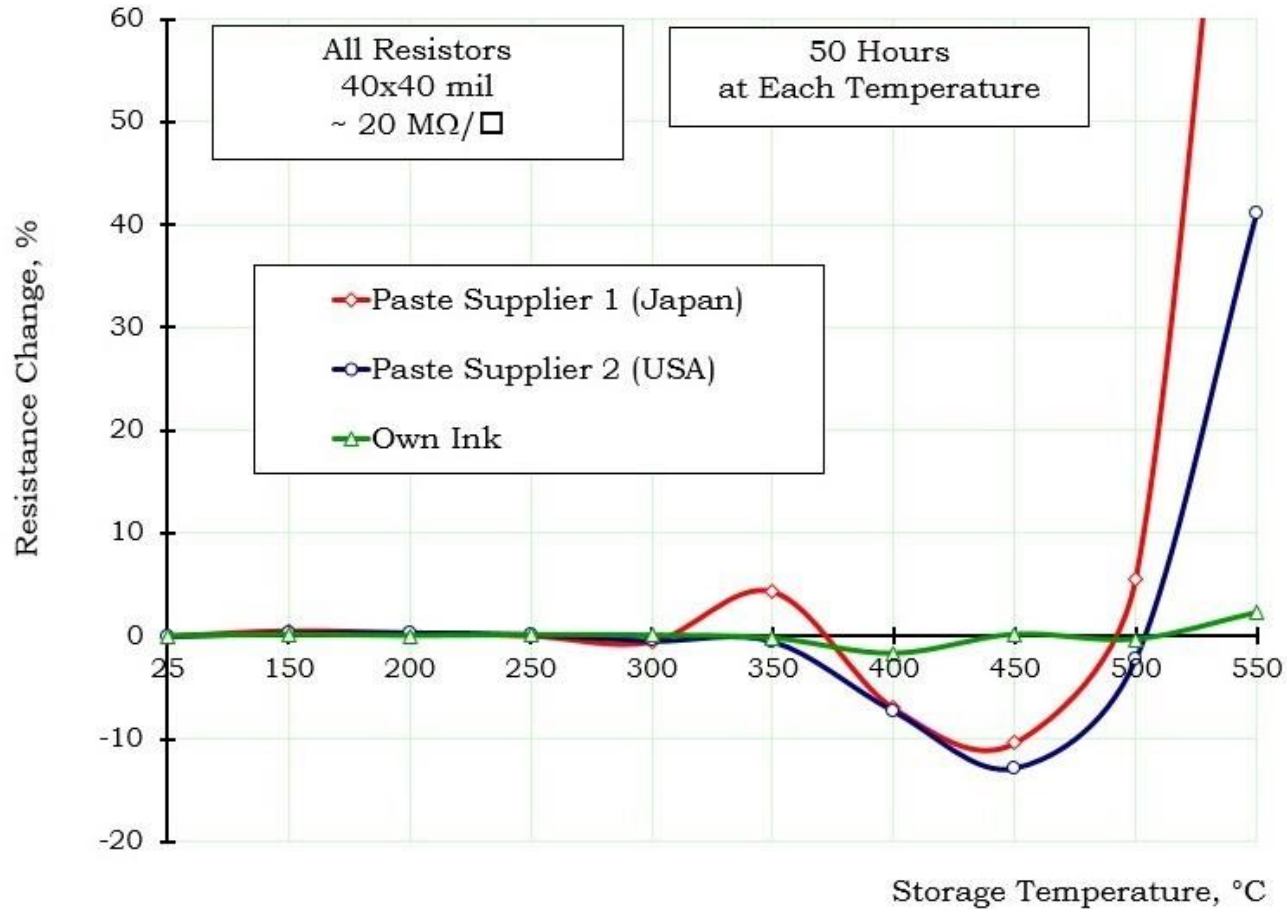
High Temperature Storage of High Ohm Value Resistors on Al_2O_3 Substrates

Resistance Change vs. Storage Temperature

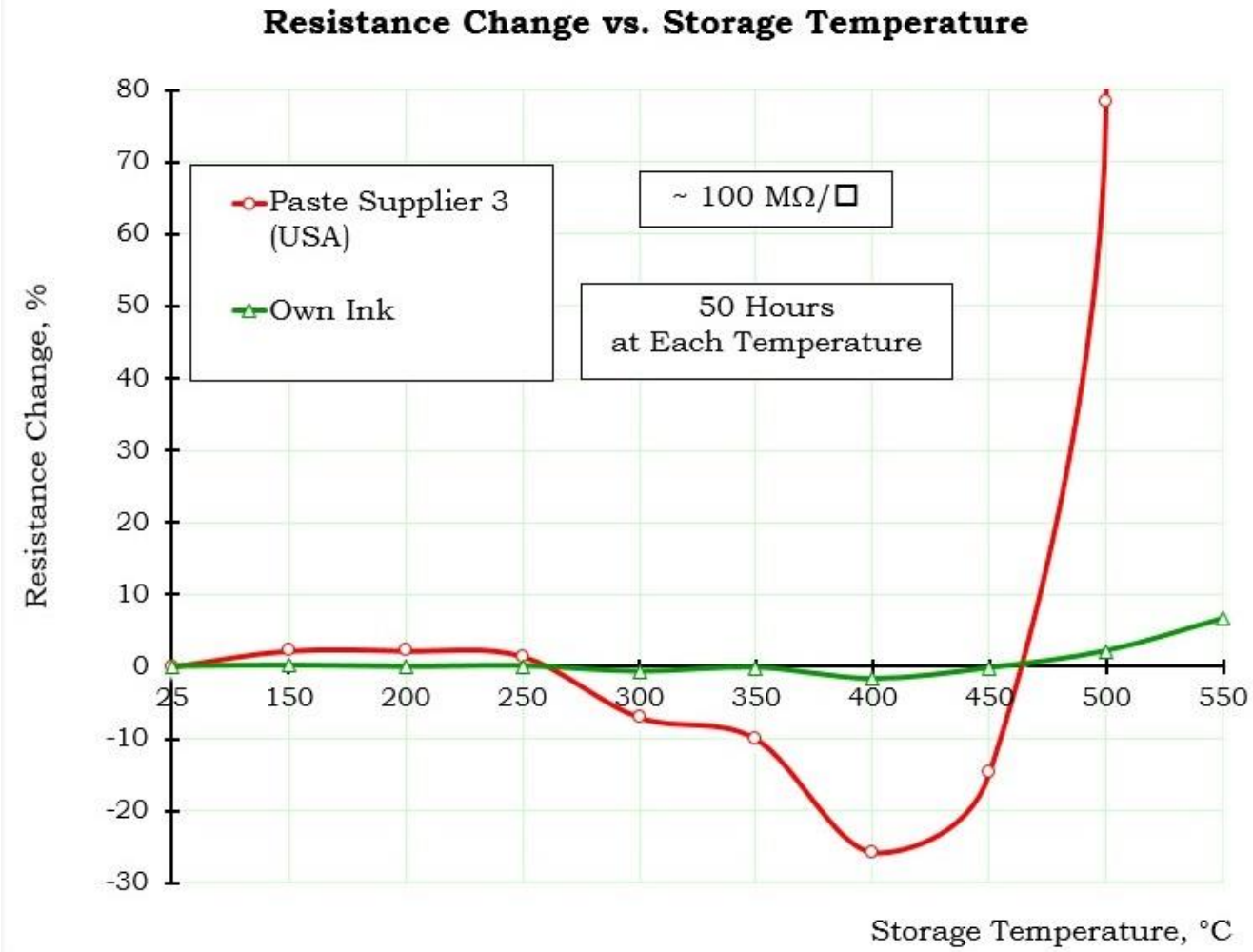


High Temperature Storage of High Ohm Value Resistors on Al_2O_3 Substrates

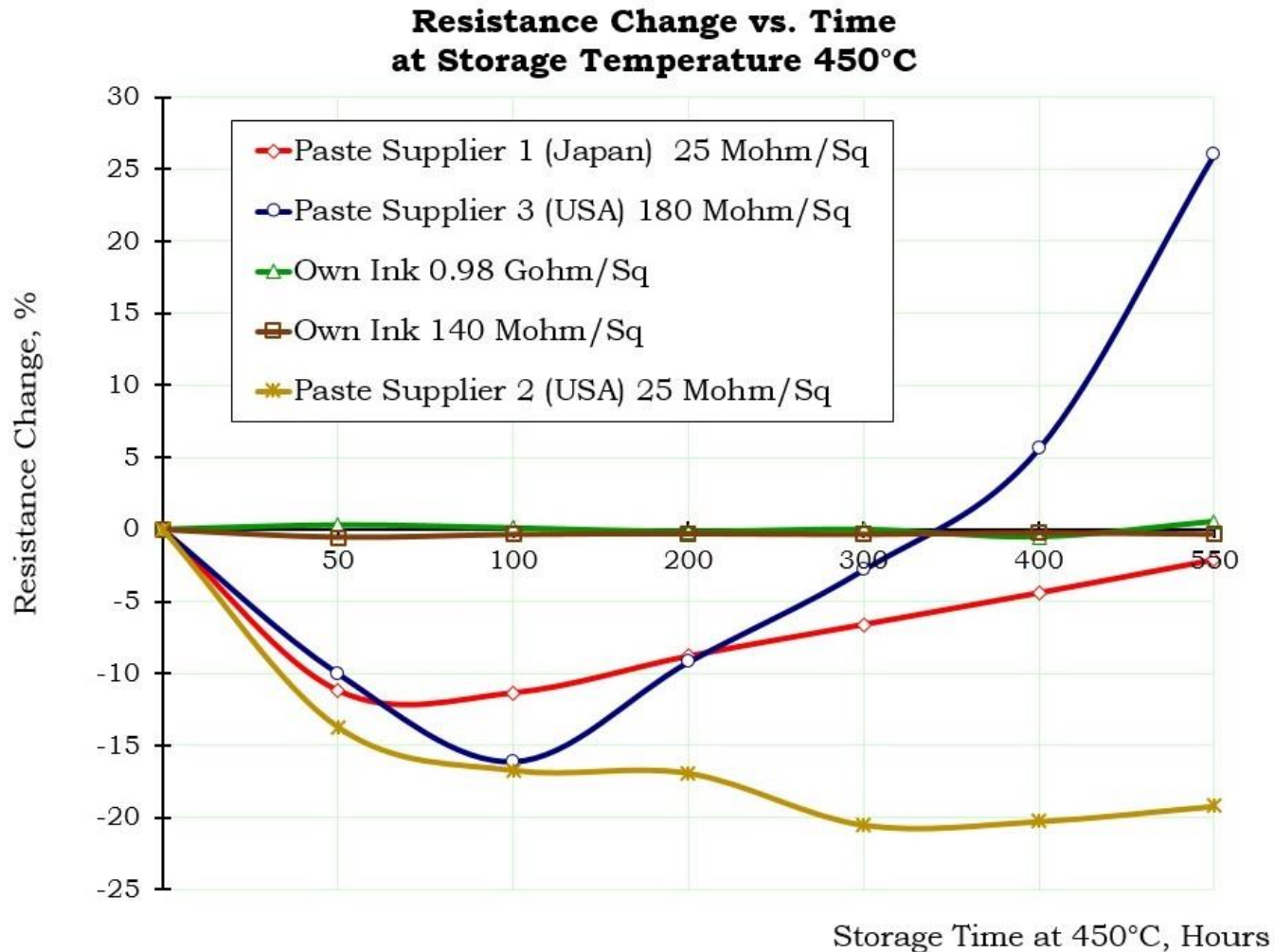
Resistance Change vs. Storage Temperature



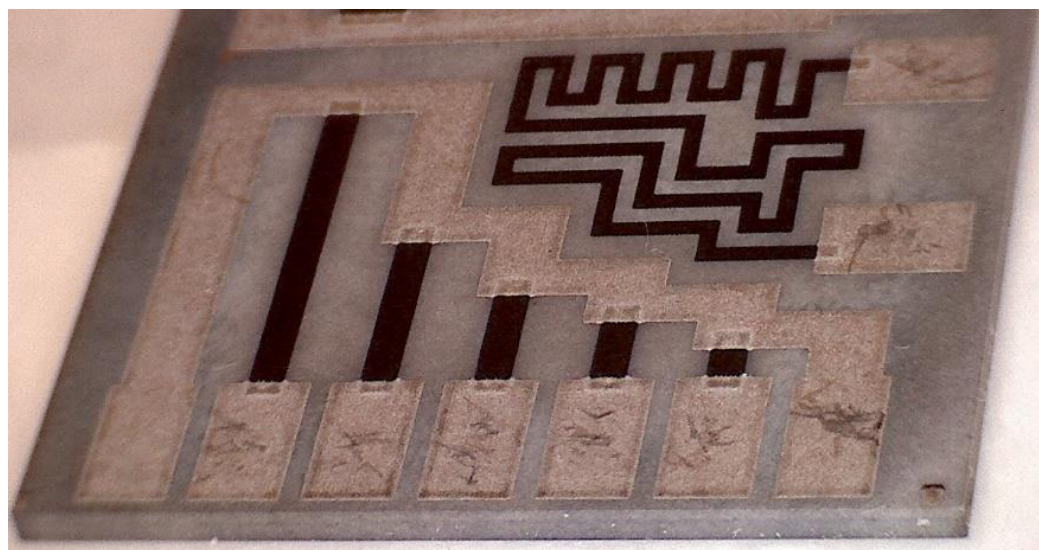
High Temperature Storage of High Ohm Value Resistors on Al_2O_3 Substrates



High Temperature Storage of High Ohm Value Resistors on Al_2O_3 Substrates



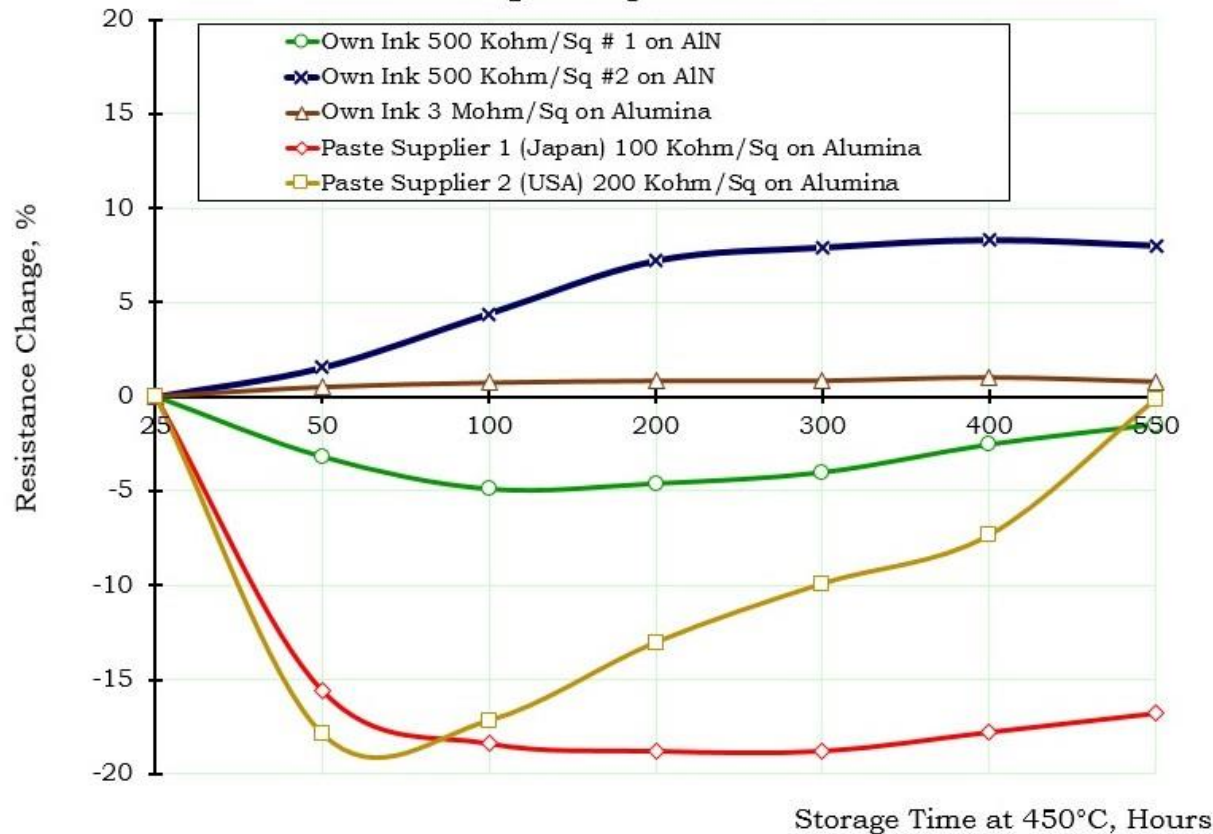
Samples of High Ohm Value Resistors on AlN Substrates for High Temperature Storage



- 500 K Ω /□ resistors on AlN
- made with ruthenium-containing conductive ceramics (RCCC)
- fired at 975°C in BTU belt furnace, 10 min at peak, 60 min total
- prepared for prolonged high temperature storage at 450°C

High Temperature Storage of High Ohm Value Resistors on AlN vs. Al₂O₃ Substrates

Resistance Change vs. Time
at Storage Temperature 450°C



Results of high-temperature storage 550 hr. at 450°C:

- 500 K Ω / \square # 1 on AlN:
⇒ negative direction of resistance shift <5%
- 500 K Ω / \square # 2 on AlN:
⇒ positive direction of resistance shift <8%
- 3 M Ω / \square on Al₂O₃:
⇒ resistance shift < 1%

As it can be seen from the results for own 500 K Ω / \square inks # 1 and #2 on AlN:

- resistance drift is controllable, may be adjusted for specific application and minimized

While the highest resistivity of commercially available inks on AlN is 1K Ω / \square , own 500 K Ω / \square on AlN has superior stability at 450°C high temperature storage test

- Novel technology of ruthenium-containing conductive ceramics (RCCC) for high ohm value resistors has allowed development of set of advanced thick film resistive inks:
 - ✓ fired in air on alumina substrates @ temperature range 900°C – 1,300°C:
 - ⇒ from 1 KΩ/□ to 1 GΩ/□
 - ✓ fired in air on AlN substrates @ temperature range 900°C – 1,100°C:
 - ⇒ from 1 KΩ/□ to 100 MΩ/□
 - ✓ firing conditions and compositions may be expanded to serve the needs of HTCC technology:
 - ⇒ firing temperature up to 1,600°C
 - ⇒ non-oxidized neutral firing atmosphere
 - ⇒ refractory W and Mo powders added in the composition for resistivity range expansion
 - ✓ directly fired in nitrogen on AlN substrates Ni/Cr/Ru series @ temperature range 950°C – 1,000°C:
 - ⇒ from 20 mΩ/□ to 20 MΩ/□

-
- The technology of ruthenium-containing conductive ceramics (RCCC) has been based on the set of non-standard concepts, approaches, and techniques :
 - ✓ unique sintering ability of composite conductive phases for resistors
 - ✓ parabolic dependence of resistivity vs. glass content with minimum values area
 - ✓ new technique for precise control of Temperature Coefficient of Resistance
 - ✓ forming of ceramic-type microstructure of high-ohmic resistors during ink firing process
 - ✓ controlled crystallization of ceramic-type high-ohmic resistors
 - High ohm value resistors based on ruthenium-containing conductive ceramics are characterized by enhanced stability at high temperature storage up to 450°C – 550°C

List of Refereed Publications

1. Moroz, M. "High Ohmic Value Resistive Inks". Proceedings of the 45th IEEE Electronic Components and Technology Conference; May 21-24, 1995; pp. 964 - 969, Las Vegas, Nevada
https://www.researchgate.net/publication/251769828_High_ohmic_value_resistive_inks
2. Moroz, M. "A New Generation of Ruthenium-based Thick Film Resistors". Proceedings of the 1996 Can-Am ISHM Symposium on Advances in Microelectronics & Packaging; Sept. 23-24, 1996; Granby, Quebec, Canada
https://www.researchgate.net/publication/272093167_A_New_Generation_Of_Ruthenium-based_Thick_Film_Resistors
3. "Thick Film Systems for Challenging Applications" given at IMAPS SoCal Technical Symposium May 12th, 2015
<http://publicationslist.org/data/M45897/ref-21/Thick%20Film%20Systems%20for%20Challenging%20Applications%20-%20Michail%20Moroz.pdf>