A Study of Factors Affecting Characteristics of Thick Film NTC Thermistors

By

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Abstract

Monolithic chip thermistors are widely used for temperature sensing and compensation in electronic industry. Over the last two decades thick film thermistors have also been utilized in a variety of applications, from automotive sensors to microwave attenuators. Rapid growth of these market segments has increased the need for better performance and more reliability from such materials. In particular, a wider resistivity range, more sensitivity to temperature change, a more predictable response, and better stability are desired. This paper examines the characteristics of a newly developed ruthenium based NTC thermistor series. The series consists of blendable members from 250 Ù/ to 100 KÙ/ . The effect of such factors as thermistor geometry and processing conditions on the above performance characteristics are presented.

Key Words: Thermistor, NTC, PTC, Sensor, Temperature Compensation, Beta, TCR

Introduction

In recent years thick film thermistors have been used in a variety of microelectronic applications. They are often utilized as temperature detectors or temperature compensating elements. A combination of NTC and PTC thermistors is sometimes used to obtain constant impedance over a specific temperature range.

Thick film thermistors offer advantages in package size and ease of integration in ceramic circuits, as well as generally lower unit cost. The growth in their utilization has been stymied, however, mostly because of lower temperature sensitivity than their monolithic counterparts. Additionally, most thick film thermistor inks which are currently available on the market require gold or high palladium content termination inks. The soaring price of palladium has further detracted from their desirability.

The current effort is directed toward making improvements in the performance and cost of thick film NTC thermistors. It also aims to provide generally useful information on factors that contribute to performance and reliability. To do so, an understanding of the principles behind thermistor behavior is necessary.

Both monolithic and thick film NTC thermistors are made of semi-conducting oxides. At first glance the resistance-temperature characteristics of such materials appear to follow no particular mathematical relationship. This is especially true about ruthenium-containing thick film thermistors. The R-T plots for low resistivity pastes appear nearly linear with a large negative slope. For higher value pastes, though, the resistivity appears to increase nearly exponentially on the cold side and drop moderately on the hot side. Applying semiconductor physics[1], however, the following expression should hold for all ideal NTC thermistors.

$$R_t = R_o e^{â(1/t_o - 1/t)} \qquad (1)$$

Where:
t_o a reference temperature
R_o resistance at t_o
â material constant
All temperatures in degrees Kelvin

This is indeed a good approximation to the behavior of most real thermistors. There are a number of material attributes which cause some deviation from this equation, as will be seen later.

Experimental

A series of blendable NTC pastes were developed using semi-conducting metal oxides, especially formulated binder glasses, and organic mediums. The formulation work was conducted using a 6:1 silver:palladium termination paste, KOARTAN 6261, and a standard 36 minute furnace profile with 10 minutes at 850°C. The NTC pastes were printed in 1 , .040"x.040", as well as 1/2 , 2 , 3 , and 5 geometries. The nominal parameters for the 1 glazed parts appear in table 1.

Table 1.

Paste Number	Resistivity Ù/	â Constant 25°C-125°C	Hysteresis %
7321	250	< -700	≤ .1
7322	500	< -1000	≤ .1
7323	1 K	< -1200	≤ .1
7324	10 K	< -2000	≤ .1
7325	100K	< -2500	≤ .3

Results and Discussion

Once the development work was completed, the effort centered on determining the functional characteristics of these materials and to answer specific questions regarding the best processing practices. More so than standard thick film resistors, NTC thermistors have porosity and open grain boundaries, needing effective encapsulation. A set of 7231 series fired coupons were covered with KOARTAN 5650 glaze, fired to 500°C, and subjected to 500 hours of aging at 150°C. The shift in resistivity upon glazing is shown in figure 1. Care was taken to maintain a temperature of 25°C ± .05°C during both sets of measurements. All resistance measurements were performed using four-point probe. The figures were nevertheless recorded quickly, to avoid minor temperature increase in the thermistor due to dissipation of electric power during measurement.

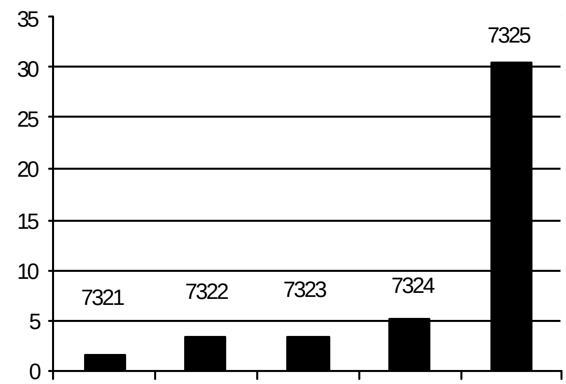

Fig. 1 Percent change on glazing at 500° C

Prior to subjecting the parts to the aging process, resistance measurements were taken on all thermistor sizes, from -55°C ±.2°C to 125°C ±.1°C. A Delta Design model 2300 chamber was used. Special baffles were constructed to keep hot air or cold gas from blowing directly on test coupons. The procedure was repeated three more times on the same parts in order to determine if there is a hysteresis.

From equation 1, the â constant can be calculated as:

$$â = \frac{\ln R_o - \ln R_t}{\frac{1}{t_o} - \frac{1}{t}} \qquad (2)$$

Equation 2 can also be expressed as:

$$\ln R_t = \ln R_o\ \hat{a}(1/t_o - 1/t) \quad (3)$$

Since $\ln R_o$ and $1/t_o$ are constants, â is the slope of a line in $\ln R_t$ vs $1/t$ plot, and therefore a constant. As a result, if t_o = 25°C=298°K, then the same value of â should be obtained for all measurement intervals between 25°C and any temperature in the range of -55°C and +125°C. In practice, however, this is not achievable because equation 1 is for bulk intrinsic semiconductors. Thick film thermistors have many grain boundaries and are constrained by the substrate. The deviation from theoretical behavior is particularly pronounced in low value thermistors, as seen in figure 2. This is because ruthenium oxide, which is used to drive down resistivity, behaves more like a metal, its resistivity going up with temperature. It also prevents the fired film from forming a very dense structure at 850°C. Figure 2 shows that even a 50 KÙ multilayered monolithic chip thermistor deviates from the theoretical description.

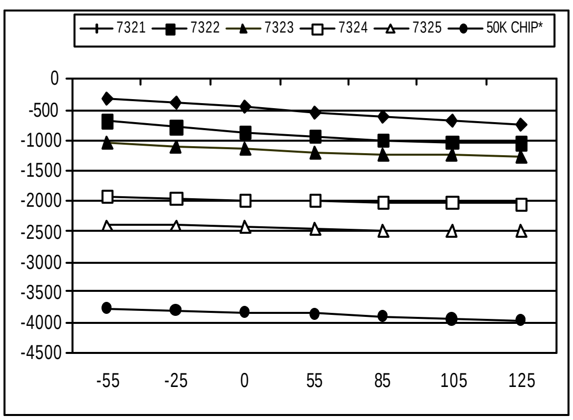

Fig 2. Change in â as a function of temperature

The data in figure 2 was obtained for the 1 geometry. The results for other sizes are somewhat different. These will be discussed in a later section along with termination effects. Figure 3 shows the percent change in â, calculated between 25°C and 125°C, after four cycles from -55°C to +125°C. The results were similar for â calculated between 25°C and other temperatures. No trend was seen in the data from previous three cycles, indicating that the changes may for the most part be due to measurement error arising from insufficient control of temperature. A deviation of ±.05°C in measuring 25°C *or* 125°C would result in .25% error in calculating â for 7325.

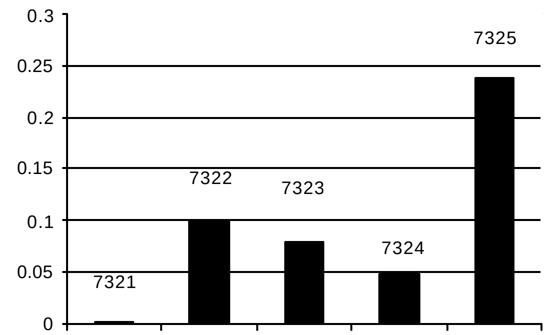

Fig 3. Percent change in â from 1st to 4th measurement

As indicated, the glazed parts were subjected to 150°C for 500 hours to measure their thermal stability. These tests were performed on untrimmed parts, since laser trimming of thermistors is difficult and usually not performed. Figure 4 shows the percent change in â, calculated between 25°C and 125°C. The after aging data was calculated for all temperature ranges shown in figure 2, and similar data as those in figure 4 was obtained.

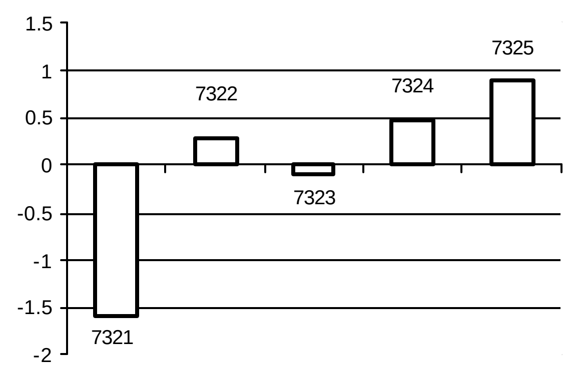

Fig 4. Percent change in â after 500 hours at 150°C.

Geometry, Termination, and Firing Effects

High palladium content inks are often recommended to terminate thermistors with. It has been shown that in fact 6:1 silver:palladium inks are suitable for many harsh applications, including under-the-hood electronics[2]. The 7321 series thermistors were formulated for satisfactory performance using a 6:1 Ag:Pd termination. It was expected that other metals would result in different resistivities and possibly different âs. While printing and firing the control group on 6:1 Ag:Pd, two more groups were printed and fired on 100% silver, KOARTAN 6111, and 100% gold, KOARTAN 4100. A comparison of resistivity and +25°C to +125°C â are shown in figure 5.

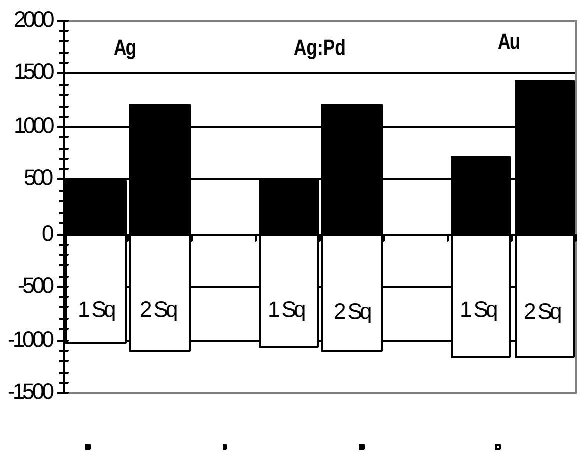

Fig 5. Resistance, top, and â, bottom, for 1 and 2 pads printed with7322.

It is seen in figure 5 that, with silver and palladium-silver terminations, the 1 pads have less than 50% of the resistivity of the 2 pads, a sign of silver diffusion. There is a corresponding decrease in â. Both terminations show slightly smaller â than their gold terminated counterparts. This should not be taken as evidence of better performance of the latter, however. When the 2 pad was printed with gold termination and 7221 thermistor, a resistance of 580Ù and â of -787 was obtained. Clearly, the 500Ù device made using silver and 7322 has a higher â than the 580Ù unit made with gold and 7321, indication that the overall composition of the thermistor has a much more pronounced effect on â than any termination effect. For this reason, it is better to design smaller pads and utilize Ag-containing termination and higher resistivity pastes or blends. By the same token, fractional square pads and even higher resistivity pastes or blends would provide additional benefits in terms of larger and less temperature dependent âs, regardless of termination material. The only draw back to this approach is that smaller units are more difficult to print uniformly, leading to a larger CV in high volume applications. Photolithographic techniques to deposit and maintain accurate spacing of the termination, and post firing the thermistor paste, should certainly help for applications that warrant this technology.

The binder glass system in the 7321 series thermistors was designed to provide efficient liquid phase sintering in a standard short 850°C furnace profile. Firing in a 60 minute profile resulted in only minor changes in resistivity and â. In most cases the resistivity was about 2-5% lower than those fired in the short profile, with about 1-2% lower â.

Conclusions

A new series of blendable NTC thermistor pastes offers a wide range of resistivity, high and predictable material constant, compatibility with low cost silver-bearing termination, and low sensitivity to firing conditions.

References

1. Sachse, Herbert B., Semiconducting Temperature Sensors and Their Applications, John Wiley & Sons, Inc., New York, 1975.

2. D. J. Nabatian, et.al., "The Wire Bondability of Silver Bearing Conductors for Automotive Applications", proceedings of 7th International SAMPE Electronics Conference, Parsippany, PP. 127-136, (1994).