THIN RESISTIVE THICK-FILM LAYERS BASED ON PRECIOUS METAL RESINATE/GLASS SYSTEMS

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This paper describes the preparation and results obtained with a ruthenium-resinate/glass resistive system prepared by firing on to a 96% alumina substrate. The results have been compared with a gold/rhodium-resinate/glass system. It is found in the ruthenium system that the particle size is about 200 Å and because of this, conduction occurs at a very low volume percent conduction phase. Temperature Coefficient of Resistance behaviour of the ruthenium based system is still anomalous.

1. INTRODUCTION

Liquid precious metals (resinates) were already used before 1900 to decorate glass and enamel. Voigt and Haeffner¹ patented these decorative materials in 1899 for making thin resistive layers on enamel.

A combination of liquid precious and base metals was used by Cockbain,² to produce 2μ-thick resistive layers on ceramic substrates. In this system the base metal-resinates provide the glass phase.

The majority of present-day resistive screen pastes are composed of metal (oxide) and glass particles, dispersed in a rheological system of resins and solvents. The thickness of the fired resistive layers is about 10–20μ.

The aim of this investigation is to compare resistivity, particle size and temperature coefficient of relatively simple precious metal resinate/glass systems with each other and with metal powder/glass systems.

2. PRECIOUS METAL RESINATES FROM NATURAL RAW MATERIALS

Chemnitius³ and Boudnikoff⁴ describe the reaction of sulfurised natural resins with precious metal salts, giving black tar-like resinates, which could be dissolved in a number of essential oils. The chemical structure of a natural resinate solution can only be roughly characterised by a number of analytical methods.

The decomposition process during firing can be followed by thermo-gravimetric analysis, which is

shown in Figure 1.

FIGURE 1 Decomposition of a mixture of several natural precious metal resinates.

Because of the present-day interest in RuO_2 -based resistive layers, we decided to compare a gold-/rhodium-resinate/glass system, investigated by Biesterbos,⁵ with a ruthenium-resinate/glass system.

3. EXPERIMENTAL

A glass powder with a specific surface area of $3\text{ m}^2/\text{gram}$, was obtained by ballmilling a conventional lead-boro-alumino-silicate frit. The frit was characterised by a density of 4.5 g/cm^3 , a softening point of 400°C and a thermal expansion coefficient of 73.10^{-7} in the region $30\text{--}300^\circ\text{C}$.

Pastes were made by thoroughly dispersing the glass particles in concentrated resinate solutions. The amount of resinate and glass were chosen so that the volume fraction of conductor (Au-Rh or RuO_2) in the fired film was between 1.5 and 10.0 vol.%. Rh-resinate is necessary to inhibit diffusion of fine gold particles. The resinate/glass pastes were applied to

96% alumina substrates by screen printing through a 325 mesh screen.

After 10 minutes firing in air at 725°C , resistive layers were obtained with a thickness between 3.1 and 4.6 micron.

4. RESULTS

In Figure 2 we have plotted the resistivities ($\Omega/\square/25\mu$) versus the vol.% Au(Rh) and RuO_2 . In order to get a first impression of TCR-behaviour, we measured the resistances of each specific layer at -55°C , $+25^\circ\text{C}$ and $+125^\circ\text{C}$. The TCR's for the regions $-55/+25^\circ\text{C}$ and $+25/+125^\circ\text{C}$ are marked on Figure 2 between brackets. The dashed lines (Figure 2) represent experimental data of Angus⁶ and Vest⁷ for various resistivities of RuO_2 crystallites ($50\text{--}300\text{ \AA}$) in lead-boro-alumino-silicate glass.

The dotted lines (Figure 2) are calculated resistivities of RuO_2 in glass, according to the theory of Scarisbrick,⁸ for random- and ordered (concentrated) dispersion of touching RuO_2 particles in glass.

5. DISCUSSION

5.1 The Au/Rh Glass System

This system, with Au/Rh particles, made from organo-metallic precursors (resinates), was investigated by Milgram⁹ and Biesterbos,⁵ who supposed that small Rh_2O_3 barriers inhibit the diffusion of $200\text{ \AA}$ gold particles.

The percolation threshold in Figure 2 (2.0 vol.%) is quite different from predicted¹⁰ and measured¹¹ values (30 vol.%) for systems with gold and glass particles of similar size.

Using 2.0 vol.% conductive particles of $200\text{ \AA}$, it is possible to cover 47% of the glass surface, which indicates that some conduction should be possible.

Au/Rh /glass films with 4 at. % Rh have positive TCR's. However in the region of 2.0 vol.% Au, the layers are unstable (probably discontinuous) with negative TCR's.

For $\text{Rh} \geq 13\text{ at.}\%$, Biesterbos⁵ made some films of about $50\text{ }\Omega/\square/25\mu$, with $\text{TCR's} < |10|\text{ ppm.}^\circ\text{C}^{-1}$, in the region $-190/+130^\circ\text{C}$.

In these films, the gold particles are supposed to be covered completely with a $10\text{ \AA}$ Rh_2O_3 barrier, which governs the electrical conduction by a tunneling process.

FIGURE 2 Resistivity of Au/Rh glass and RuO_2 /glass systems.

5.2 The RuO₂/Glass System

A 50% coverage of the glass at a percolation threshold (Figure 2) of 1.0 vol.%, is realised by 90 Å RuO₂ crystallites. Our resistivities for vol.% RuO₂ ≤ 5%, are 20–300 times lower than values realised by Vest⁷ with 60 Å RuO₂ crystallites. For this reason, our crystallites should be smaller than 60 Å. There are, however, indications that the particle size is about 200 Å, which means that we are probably dealing with a different coverage of the glass surface, according to Scarisbrick.⁸

RuO₂ films with 10 vol.% conductive phase show a much higher resistivity and lower TCR than corresponding Au/Rh glass films, with respect to resistivities and TCR's of bulk materials. Either the RuO₂ particles have different properties to the bulk material, or contact between two particles is different from the situation in the gold/glass system.

The presence of an unknown barrier between two RuO₂ particles is also possible. This barrier differs from the Rh₂O₃ type, since TCR's in the RuO₂-glass system are strongly dependent on the temperature.

6. CONCLUSIONS

It is possible to create interesting resistive metal/glass films of about 3.5 micron thick, with Au/Rh and Ru resinate, together with lead-boro-alumino-silicate glass-powder. Thanks to the large number of 200 Å conductor particles, conduction occurs at a low vol.% conductive phase. The TCR-behaviour of the RuO₂/glass system is anomalous.

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