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ENAMELLED STEEL SUBSTRATES FOR PRINTED CIRCUITS

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The preparation of steel substrates coated with intermediate ground and final ceramic coatings is described. The basic material for the preparation of both coatings is the same kind of special glass. The coatings were thermally treated up to 960°C. The resulting substrates were tested for the usage in thick film technology by applying ruthenium resistor compositions designed for use on ceramic substrates. The resistors were fired up to 900°C and their resistance and TCR were measured. They showed almost the same dependence on firing temperature as the resistors printed on alumina substrates. The TCR was only shifted towards more positive values.

1. INTRODUCTION

Papers presented by S.J. Stein and R.B. Schabacker at the European Hybrid Microelectronics Conference in Ghent (May 21-22-23, 1979) showed a rapid growth of interest in enamelled substrates.[1,2] This interest is especially understandable due to the present trend in technology in hybrids being more and more centred on the use of non-precious metals, new substrate materials and new lower cost techniques.

In 1979 we succeeded in preparing protective coatings on steel[3] with exceptional properties which could be presumed to be suitable for the preparation of insulated steel substrates, applicable for heat treatment up to temperatures above 800°C. We tried to prepare new types of steel substrates coated with ceramic materials and to test them for the preparation of thick film resistors printed by means of ruthenium based systems designed for use on ceramic substrates.

2. PREPARATION OF ENAMELLED STEEL SUBSTRATES

2.1 *Intermediate ground coating*

The coating created on steel sheets by means of special glass marked EV 201 formed the ground for the preparation of substrates coated with a ceramic film. The composition of the respective glass is indicated in patent applications.[3,4]

The main preparation of the ground coating is as follows: finely ground glass frit is applied in a thin uniform film to a steel sheet by the method of electrostatic spraying or by simple dusting of dry glass powder on a steel sheet coated with a very thin oil film, and eventually by some other methods (see Figure 1).

After drying, the glass coating is fired for several minutes at temperatures ranging from 780° up to 960°C in a furnace. During the firing the glass covering the steel melts at first, thus creating a thin glossy glass film, which prevents scale forming. Should the temperature overreach 780°C, a reaction occurs among glass, iron and oxygen, creating a film on steel having other properties which are as follows:

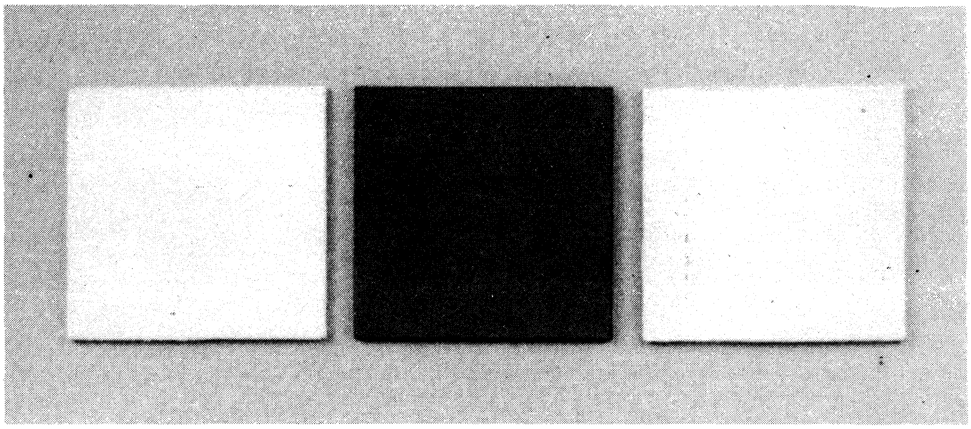

FIGURE 1 Steel substrates coated with (from the left) glass powder, ground coating and final ceramic coating.

1) The coating is dull till folded as per the amount of glass powder applied to the steel surface (see Figure 2). Due to this reason, the thickness of the coating is difficult to determine. Its colour changes from dark grey to light grey according to the firing temperature. The melting temperature of the coating is not estimated but it is higher than 1,100°C.

2) The coating is partially ingrained in the substrates and adheres exceptionally well to steel and it cannot be removed in a simple way. The coating does not peel even during

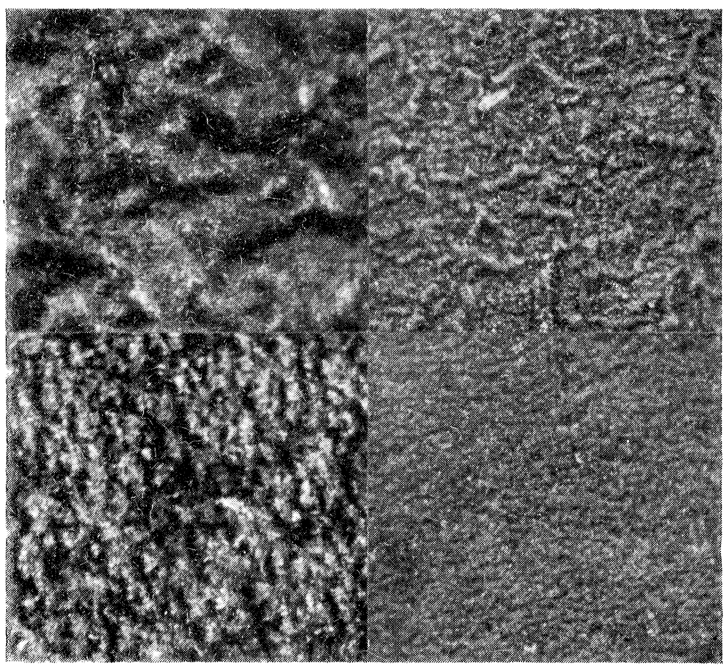

FIGURE 2 Micrographs of ground coatings (35x).

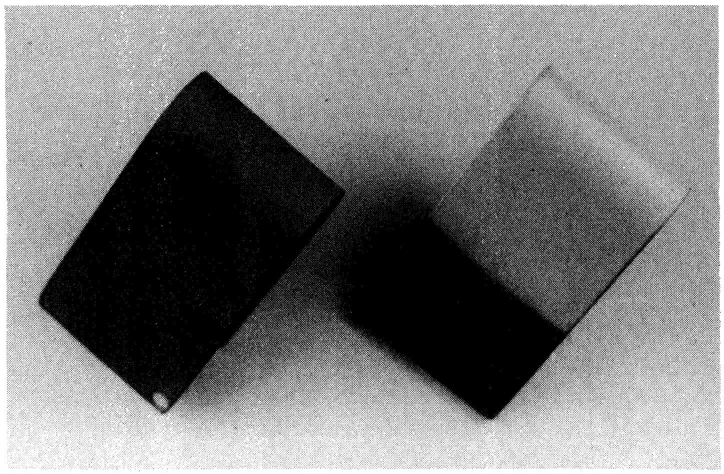

FIGURE 3 Steel sheets coated with a ground coating and also with a varnish and then bent.

sheet bending (see Figure 3). Only microscopic cracks are created but they cicatrize by refiring or local heating. The coating is resistant to damage even when subjected to quick cooling down from the temperature of 700°C by submersing in water.

3) The ground coating is also well resistant to some acids. For instance nitric acid did not cause any apparent changes in the coating during a period of four weeks.

4) Coated substrates can be subjected to multiple firing cycles in the air at least up to the temperature of 880°C without causing any peeling of the coating.

5) The coating protects steel against corrosion to a certain degree. Varnish and enamel of various kinds can be applied easily to the ground coating adhering to the surface exceptionally well (see Figure 3). Any varnish or enamel not adhering well to this coating would be discernible.

6) The electrical resistance of the coating depends on the firing temperature and the firing time, and can reach values up to 10^9–10^{10} ohms between the 0.5 mm × 0.5 mm electrodes. Breakdown voltages vary between 200 up to 300 V.

7) Should glass powder be mixed with ZnO powder before being applied to the substrate, a film is created after the firing which has similar properties as those of the previous case, with the exception that its electrical resistance is considerably lower and amounts to about 4 kohms between the electrodes.

8) When firing at lower temperatures (720°C), a glossy film is created. In spite of the fact that the film created by the above method shows a relatively high electric resistance, it cannot be used for applying metal films, the latter requiring another heat treatment. The coating is crystalline and during the heating a diffusion of metal occurs along the crystalline grains towards the steel core. This causes a short circuit between the steel core and the applied metal film. It is obvious that it is necessary to apply another film to the ground coating in order to prevent the above diffusion of conductive particles. Enamels are preferred which, however, permit firing temperatures below about 675°C only.

2.2 *Final ceramic coating*

To create the final insulating coating of the steel substrates dielectric compositions (e.g. Du Pont 9950) were applied to the ground coating by the screen printing method

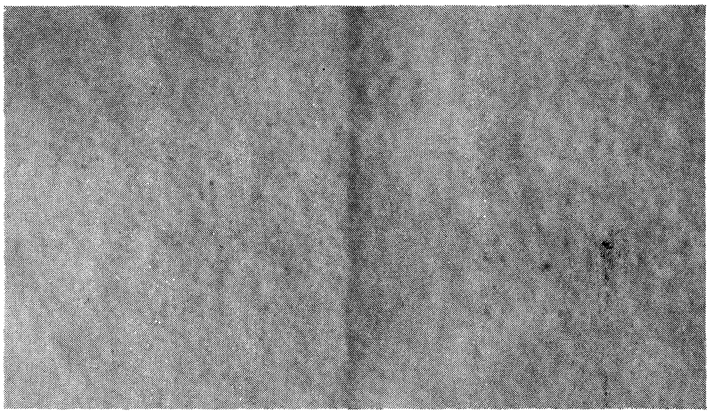

FIGURE 4 Micrograph of a final ceramic coating (3 and 4 films) (35x).

and then fired at 860°C. It showed that these created coatings, having a suitable thickness, allow further firing up to 860°C. However, it proved that the created coatings peeled at the edge of the substrate.

Due to this reaction another paste was prepared containing again EV 201 glass and Al_2O_3 powder in various ratios and liquid vehicle. This composition was printed, its film thickness being 15 microns, and then fired at peak temperature ranging from 780° up to 960°C for 1-20 minutes at peak. The total thickness of the coating was changed by multiple printing, varying up to 60-80 microns.

The ceramic insulated steel substrates created have the following basic properties:

1) The coating is grey-white till white-grey in relation to the mixture proportion – glass + Al_2O_3 – which can be varied from 10 wt% up to 100 wt% glass and from 0% up to 90 wt% Al_2O_3. When the glass content is from 100 wt% up to 40 wt% a glossy coating is created. When the Al_2O_3 content is increased the fired coating starts to show ceramic properties. The quality and smoothness of the surface depends on the method of application. When using the screen printing method, a relief is formed by the screen, or another slightly uneven surface can be seen (see Figures 4 and 5).

2) After firing, the final coating joins the ground coating very well, so that the substrates can be heated many times at least up to 860°C without damaging the coating.

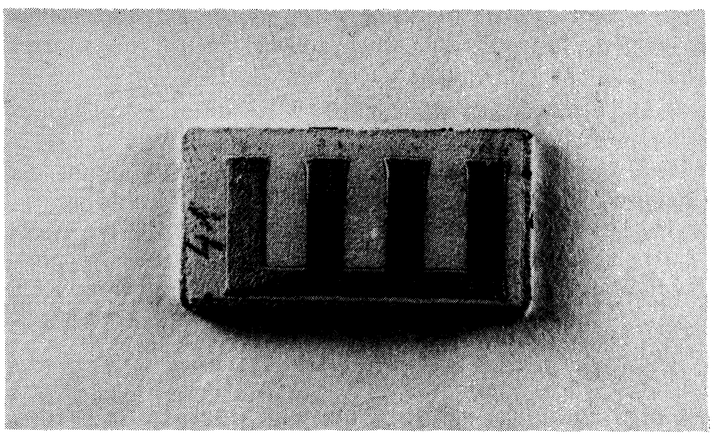

FIGURE 5 Resistor test pattern.

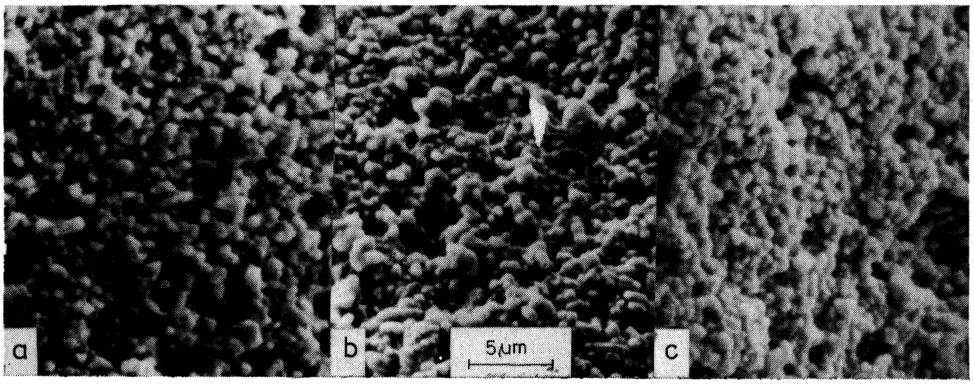

FIGURE 6 Scanning electron micrographs of final ceramic coatings. a) 15 wt% glass + 85 wt% aluminum oxide, b) 20 wt% glass + 80 wt% aluminum oxide, c) 25 wt% glass + 75 wt% aluminum oxide.

3) The electrical resistance between the 4 mm x 3 mm gold pads and the steel core reaches the values up to 7.10^{12} ohms (for two or three printed films) and it does not vary even after the refiring.

4) The breakdown voltages vary according to the number of applied films from 400 V for double film up to 1000 V for triple film.

5) During the firing process, Al_2O_3 areas are coated with glass in which Al_2O_3 solutes partially and interjoin with one another, thus creating a relatively compact coating (see Figure 6).

3. ELECTRICAL PROPERTIES OF RESISTORS

Some kinds of resistor compositions based on ruthenium compounds (especially Du Pont 1461 and 1411 series and our compositions marked No 11 and No 41) were selected for the preparation of thick film resistors. The resistors were printed on alumina and the above mentioned enamelled (ceramic insulated) substrates were provided by Au terminations, then dried and fired at peak temperatures ranging from 820° up to 900°C for 10 minutes at peak. The total cycle time was 45 minutes. The dimensions of the resistors were 4 mm x 2 mm and their dried film thickness amounted to 25-28 microns (see Figure 5). The composition containing 15 wt% glass and 85 wt% aluminum oxide was used to prepare ceramic coating.

The electrical resistance and the temperature coefficient of resistance of the prepared resistors were measured. Figure 7a shows the sheet resistance as a function of peak firing temperature for resistors printed on enamelled steel substrates (full lines) and on alumina substrates (dashed lines) for four resistor compositions mentioned above. The sheet resistance of the resistors printed on enamelled substrates by using DP 1461 series is about two times higher than that of the resistors printed on alumina substrates. However, the respective curves are only shifted in relation to one another (see curves 1 and 1').

A similar behaviour was found with resistors prepared from the compositions DP 1411 and No 11. Difference between the substrate types is approximately 25% maximum with higher resistance on alumina substrates (see curves 2-2' and 3-3'). The resistors prepared from composition No 41 show a higher difference in resistance values (see curves 4 and 4').

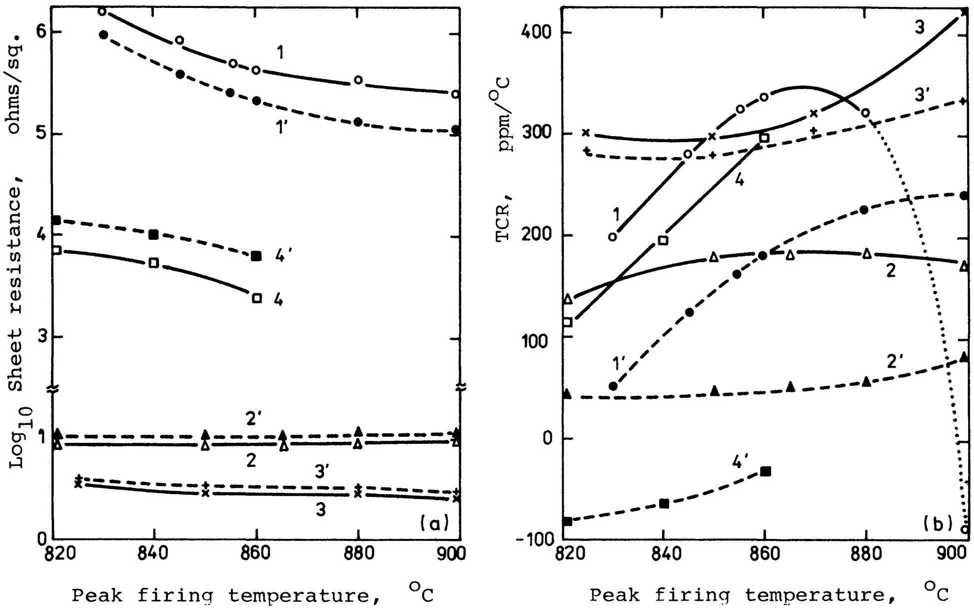

FIGURE 7 Sheet resistance (a) and TCR (b) vs. peak firing temperature for resistors screen-and-fired on enamelled steel (full lines) and alumina (dashed lines) substrates for DP 1461 and 1411 series (curves 1-1′ and 2-2′, resp.) and for compositions Nos 11 and 41 (curves 3-3′ and 4-4′, resp.).

The dependence of TCR of resistors printed onto alumina substrates (dashed lines) and of those printed onto enamelled steel substrates on the peak temperature shows that the respective curves are shifted in relation to one another. The enamelled steel substrates show more positive values (see Figure 7b, full lines). The extent of the shifting depends on the applied resistor composition. The TCR of 1461 resistors on enamelled substrates is higher about +160 ppm/°C up to the peak firing temperature of 860°C. With higher temperatures, the TCR reaches the maximum at about 870°C, and decreases quickly down to negative values (see Figure 7b, curve 1). It cannot be excluded that at a high temperature a certain reaction of the resistor composition with the substrate may occur.

The TCR of DP 1411 resistors on enamelled substrates is higher, about 130 ppm/°C (see curves 2 and 2′). In the case of a very low resistor composition No 11, the difference in TCR is still lower about 25 ppm/°C (see curves 3 and 3′). A higher difference in TCR is observed for both kinds of substrates for 10 kohms resistors.

Furthermore a long term resistor stability results. It shows that the resistance change at 150°C after certain time is practically the same for resistors printed on both types of substrates. In some cases the resistance stability of the resistors printed on enamelled substrates is even higher.

4. CONCLUSION

The performed experiments have shown that steel substrates coated with ceramic insulating coating can be prepared which are suitable for printed resistors even when applying resistor compositions designed for the use on ceramic substrates. The difference lies precisely in the fact that the resistance values are shifted towards higher or lower values in relation to the kind of applied resistor composition. This fact is obviously influenced by the surface state. Enamelled steel substrates laboratory prepared by us have not such a smooth surface as that of alumina substrates. The surface characteristics are influenced also by a composition of the paste (by the ratio of glass and Al_2O_3) applied to the ground coating. Furthermore these resistors differ from those printed on alumina substrates by their temperature coefficient of resistance which is shifted to more positive values in all the cases of used resistor compositions. Such a behaviour can be explained by higher thermal expansion coefficient of enamelled steel substrates compared to that of alumina substrates, as it has been reported in the paper.[5]

In order to reach a lower value of TCR, it is probably sufficient to reduce the content of components in the resistor compositions having positive TCR.

Steel substrates coated with ceramic insulating coating can be easily prepared even under laboratory conditions. It is sufficient to apply a suitable kind of glass, e.g. EV 201, and a suitable mixture of glass and Al_2O_3. The preparation of all the substrate with its intermediate ground and final coatings takes only about 20 up to 30 minutes, because neither heating nor cooling during firing cycles need to be performed slowly. The creation of the suitable ground coating on steel is the most important step for the preparation of enamelled steel substrates of the studied type.

The suggested type of enamelled steel substrates will find a good application in hybrid electronics.

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