Set up of a Screen-Printing Procedure for the Production of a β Alumina-Based Gas Sensor*

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Abstract. A gas sensor based on a β-alumina thick film was recently developed on a laboratory scale. This sensor can be successfully used for selective detection of CO and NO_x, resulting from an appropriate choice of the working temperature of the sensing element. This paper deals with the approach of the industrial transfer of the sensor prototype, mainly concerning the scale-up of the screen-printing procedure from a hand-operated apparatus to an industrial production machine. Many parameters were already investigated during the laboratory development, namely the ink composition in terms of organic/inorganic component ratio, the type and amount of the liquid dispersant and rheological agent, the composition and softening temperature of the binder, the β-alumina/binder weight ratio. During the industrial transfer, some other parameters must be considered, such as the particle size distribution of the ceramic components of the ink, the influence of the mesh number of the screen fabric on the surface texture of the β-alumina film, the viscosity performances of the ink as a function of the applied shear rate and ageing. A common commercial metallic paste was also used as reference for optimizing the characteristics of the β-alumina based ink.

Keywords: screen printing, thick films, gas sensor, ink viscosity, beta-alumina

1. Introduction

Within an European Community Brite-Euram project (ECONOX I, BE 7058/1994–1997), a new sensing device using SO_2 pre-treated β-alumina as sensing material was developed for the detection of CO, NO and NO_2 [1,2]. The gas pre-treatment yields a sodium sulphate film which becomes a part of the ionic conductor. The sensor uses the electrochemical properties of these solid electrolytes associated with two electrodes with different catalytic properties, one made of platinum, the other of gold, which are in contact with the same gas mixture. More details on the sensing mechanism and sensor design have been already published in this journal [3].

The sensor prototype was obtained by firstly screen printing a β-alumina based ink on an α-alumina substrate, followed by the deposition of a platinum heater (on the other side of the α-alumina substrate) and of the two metallic (Pt, Au) electrodes on the β-alumina film. The SO_2 pre-treatment is the final preparation step.

On this ground an industrial application of this prototype is now supported within the Brite-Euram project ECONOX II (BE-97-4028, 1997–2000), mainly in view of its use for car exhaust analysis. One of the first steps of the industrial transfer of this sensor prototype concerns the scale-up of the screen-printing of the sensitive element, the optimization and standardization of the deposition procedure and ink parameters and the main results achieved during this development are presented in this paper.

2. Experimental Procedure

The β-alumina powder was prepared by a sol-gel method, hydrolyzing aluminium isopropoxide in an aqueous solution of sodium oxalate at 80°C. The hydrolysis conditions led to a random packing of colloidal aluminium hydroxide flocks. Their surface, negatively charged, preferentially adsorbs positive ions, like Na^+. After drying in the mother liquor, the amorphous precipitate crystallized at about 1115°C, as evidenced by thermal analysis (TG-DTA; Netzsch STA 409; heating rate of 10°C/min) [4,5]. In this work, the amorphous powder was calcined at 1200°C for 30 min in order to obtain a well-crystallized product, showing a negligible residual weight loss. The final product was identified by X-ray diffraction (XRD, Philips PW 1730, Cu Kα) as a mixture of β and β'' alumina (JCPDS files 31-1263 and 31-1262, respectively) [4]. After calcination, the powder was significantly aggregated: a grinding step was thus performed in a planetary (Retzsch PM4) or in an attrition (Netzsch Molinex) mill. The particle size distribution of the ground powder was analyzed by laser granulometry (Malvern Particle Sizer 3600D).

The screen-printing ink was then prepared by mixing the β-alumina calcined powder with the three classic components [6,7]: a binder, a liquid dispersant and a rheological agent. Considering the operating temperature range of the sensor (300–700°C), an organic binder or an inorganic one with a low softening point (mainly based on borosilicate glasses) [6,7] were inappropriate: a sodium aluminosilicate glass was then synthesized by quenching in water silica, α-alumina and sodium carbonate mixture fused at 1000°C. The composition of the glass (NaO/$(Al_2O_3 + SiO_2)$ weight ratio of about 1:3) was chosen in order to have the lower softening point consistent with the sensor working conditions (a softening point of about 780°C was obtained). In addition, the glassy phase remains as a component of the sensitive film, preferentially located at the β-alumina grain boundaries, as observed by SEM (Fig. 1). Therefore, its influence on the electrical response of the sensitive element cannot be under-estimated: the relative high sodium oxide content allows to obtain a certain electrical conductivity of this glass ($\sigma_{300°C} = 5.4 \cdot 10^{-6}\Omega^{-1}$ cm^{-1}) [8].

After milling, this glass was mixed with β-alumina in an alcoholic suspension in a ball mill. Many mixtures having different β-alumina/glassy binder
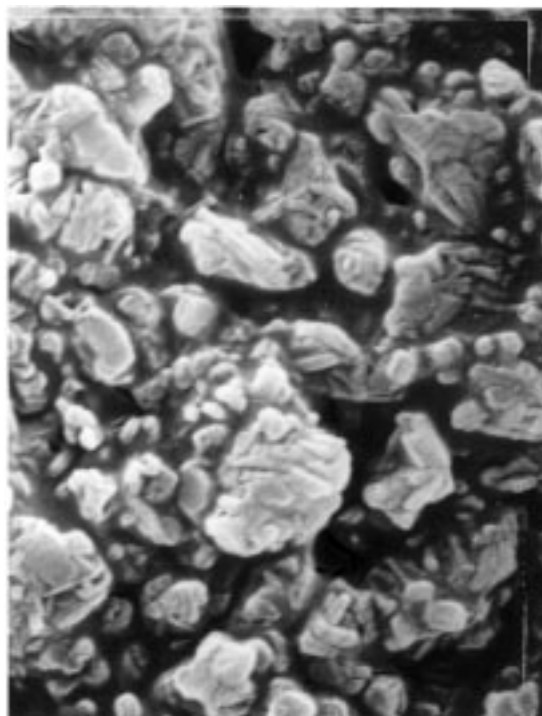

Fig. 1. Microstructure of a screen-printed ink: β-alumina grains surrounded by the glassy phase (2.9 cm = 5 μm).

weight ratio were prepared. In this paper the results are mainly referred to a 60:40 weight ratio mixture.

A mixture of diethylene glycol monobutyl ether and terpene alcohol, having a boiling point of about 200°C and a vapour pressure <1 mmHg at 20°C, as a liquid dispersant, and a copolymer poly(vinyl butyral − vinyl alcohol-vinyl acetate) (average molecular *weight* = 50,000 − 80,000; $T_g \approx 70°C$), as a rheological agent, were also mixed with the inorganic powders in a ball mill for 24 h. The relative amounts of the different components were chosen on the ground of viscosity measurements (Brookfield HB-DVII+ rotational viscometer with small sample adapter SC4 − 14/6R, at 25°C±0.2°C), using a commercial conductor ink (PdAg 5103, Du Pont Electronic Materials, USA; composition: Ag/Pd = 3:1; glass frit conductor ink with low lead and cadmium content and nickel oxide free) as a reference. The viscosity performances of the inks were investigated as a function of applied shear rate (ranging between 0.4 to 40 s^{-1}, corresponding to spindle speeds between 1 to 100 r.p.m. respectively), time (at a constant spindle speed) and of the ageing of

the ink (taking in account that a commercial ink has an optimum lifetime of about 1 year).

A hand-operated (Progem, Italy) and an industrial automatic (MOD.A1, Baccini, Italy) screen-printing machines with different fabric mesh screens were used to deposit square-shaped thick film patterns with an area of about $0.4 \, cm^2$ on α-alumina substrates. Standard stainless steel wire cloth screens were used, as generally made in the industrial production owing to their mean lifetime (about 50,000 screen-printing runs). Mesh fabrics are commercially designated by a mesh count, which indicates the number of openings per linear inch (25.4 mm). The higher the number, the finer the mesh fabric. The mesh count is in close relation to the wire diameter (d) and the mesh opening (W): for a given count, $d + W$ is constant and the wire diameter can vary to a small extent.

Several different screens were used, as reported in Table 1, in order to investigate the influence of the mesh number on the smoothness of the deposited film. In fact, it must be reminded that one of the critical steps of the prototype production is the deposition of the platinum and gold electrodes (by sputtering or screen-printing) on the β-alumina thick film: therefore, the adhesion and the electrical contact should be strongly influenced by the surface quality of the deposited film.

The 400 mesh cloth is the finer commercially available one. Industrial production of the sensor using this screen is not expected, due to its short lifetime in printing hard ceramic powders. However, many tests were performed using this cloth as a reference. The thickness of the screen-printed films mainly depends on the type of photographic emulsion covering the screen. All the screens for the automatic machine were thus covered by the same emulsion film (CDF4, Ulano Intern. Inc., USA, thickness $= 40 \, \mu m$) for producing films with an almost constant thickness.

After drying in air at room temperature, the films were fired at 900°C (soaking time of 2 h). The heating and cooling steps were controlled in such a way as to limit crack formation induced by the decomposition of the organic components and by the inhomogeneous shrinkage of the screen-printed film. Particularly a very slow cooling rate (1°C/min) was adopted between 900°C and 700°C, that is in the softening temperature range of the glassy binder.

The morphology and the thickness, on cross-sections, of the screen-printed films were then observed by scanning electron microscopy (SEM, Hitachi S 2300), while the phase evolution due to the possible chemical interaction between β-alumina and the sodium aluminosilicate glass was investigated after firing by XRD.

3.   Results and Discussion

3.1.   Particle Size Distribution of the Ceramic Components

Two different comminution procedures were compared: the particle size distribution of the β-alumina/glassy binder mixture milled in a planetary or in an attrition mill are reported in Fig. 2.

The lower mean particle size $(<1 \, \mu m)$ and the narrower particle size distribution of the powder milled by the attritor are both significant parameters in optimizing the dispersion of the glassy binder with the β-alumina powder, in improving the homogeneity of the film composition, its smoothness and also its adhesion to the α-alumina substrate. In fact, attrition milled mixtures having a β-alumina/glass weight ratio of $80:20$ presented the same adhesion performances of planetary milled mixtures having a ratio of $60:40$, as indicated qualitatively by the resistance to a simple "Scotch-tape test". In addition, the lower particle size distribution can also allow an easier deposit through high mesh number fabrics.

Table 1. Specifications of the stainless steel screens

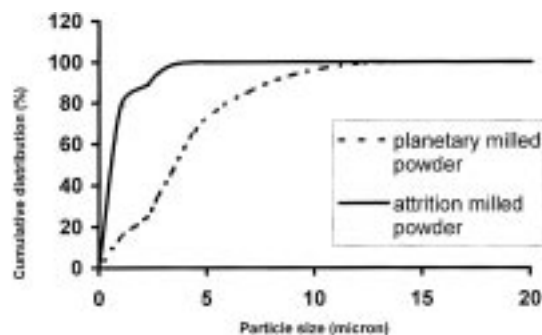| Designation/type of screen-printing machine	No. wires/cm	No wires/inch (mesh no.)	Wire diameter (d) (mm)	Mesh opening (W) (micron)
SD 200/90 Hand-operated	34	88	0.09	200
SD 90/40 Automatic	77	200	0.04	90
SD 50/30 Automatic	125	325	0.03	50
SD 40/25 Automatic	154	400	0.025	40

Fig. 2. Particle size distribution of the β-alumina/glassy binder mixture after planetary or attrition milling.

3.2. Screen-Printing Ink Composition

The composition of the ink was set up by optimizing its viscosity as compared to a reference commercial ink. As a function of the particle size distribution of the ceramic powder, the rheological agent amount ranged from 0.01 to 0.1 g/g of ceramic powder, while the powder/liquid dispersant ratio was changed between 2 : 1 and 1.5 : 1.

The viscosity of an ECONOX ink (β-alumina/glass weight ratio of 60 : 40; planetary milling) and of the reference one are compared as a function of different spindle speed in Fig. 3 and as a function of time at a constant spindle speed (20 r.p.m.) in Fig. 4.

Typical shear-thinning behavior is presented by both inks and their curves are quite well super-
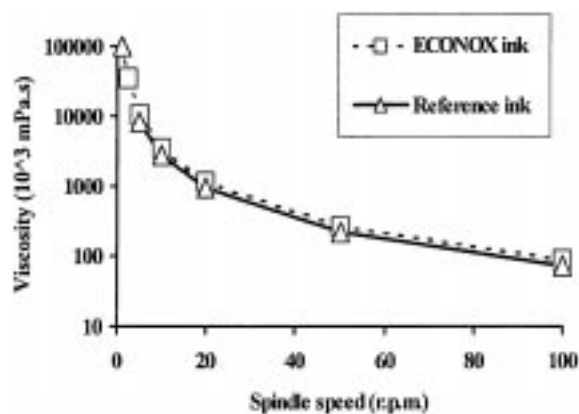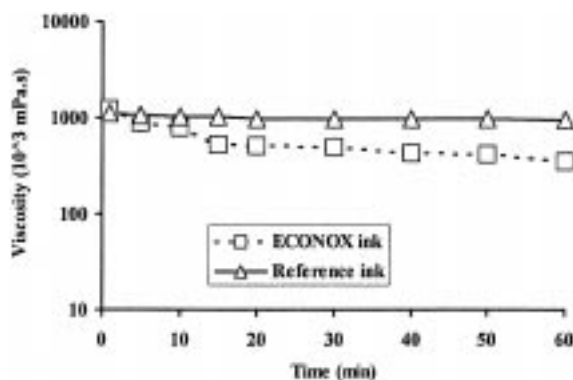

Fig. 4. Comparison between the viscosity of an ECONOX ink and of a PdAg reference ink as a function of time at a constant spindle speed (20 r.p.m.).

imposed. The most significant differences are evidenced in Fig. 4, where the viscosity value of the commercial ink becomes immediately stable at constant shear rate, whereas it takes 15 min for the ECONOX ink. This ink is therefore slightly thixotropic, since after a rest, when a strain rate is applied suddenly and then held constant, its apparent viscosity is a diminishing function of the time of flow. In addition, the ink recovers its initial state after a certain interval at rest [9]. These rheological properties should allow an easy printing of the ink through the screen under the squeeze pressure and a fast (few minutes) settling of the film on the substrate without bleeding or smearing from the defined geometry [10].

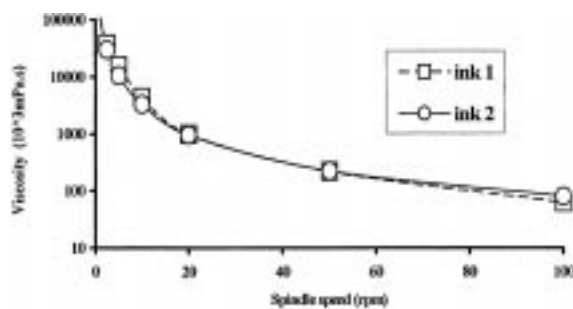In Fig. 5 the viscosity of two ECONOX inks which are different in β-alumina/glass weight ratio and in the

Fig. 3. Comparison between the viscosity of an ECONOX ink (β-alumina/glass weight ratio: 60 : 40; planetary milled) and of a reference PdAg commercial ink, as a function of the spindle speed.

Fig. 5. Comparison between the viscosity curves of two ECONOX inks (ink 1: β-alumina/glass weight ratio = 60 : 40; planetary milled; ink 2: β-alumina/glass weight ratio = 80 : 20; attrition milled).

milling procedure used are compared. A suitable modification of the inorganic/organic ratio in the ink allows for a similar viscosity performance.

The viscosity characteristics of the ECONOX ink were also determined after one year from its preparation (Fig. 6), i.e., the generally accepted lifetime of a commercial ink. It can be clearly noted that the viscosity was not significantly affected by the ageing of the ink, which could induce changes due to evaporation of the liquid dispersant or an increase in polymerization of the rheological additive.

3.3. Characterization of the Screen-Printed Films

Using the hand-operated machine equipped with a low mesh number screen, highly rough films (Fig. 7) having a mean thickness of about $100 \mu m$ were produced, with significant changes from one point to another. The thickness ranged between about $70 \mu m$ (in the middle of the mesh opening) to about $130 \mu m$ (corresponding to the wire positions) These values are referred to the films after firing at $900°$.

Transfer to the automatic machine and the use of lower mesh number clothes produced a significant improvement in the smoothness of the film (Fig. 8). The thickness had a mean value of about $40 \mu m$ with a range between 30 and $50 \mu m$. An example of a SEM cross-section view of the films is presented in Fig. 9. In addition, it was observed that the thickness of the film was mainly linked to the nature of the emulsion which covered the screen and not to the type and composition of the ink. If a higher thickness was required, it was necessary to superimpose the deposits. By SEM observations it was estimated that
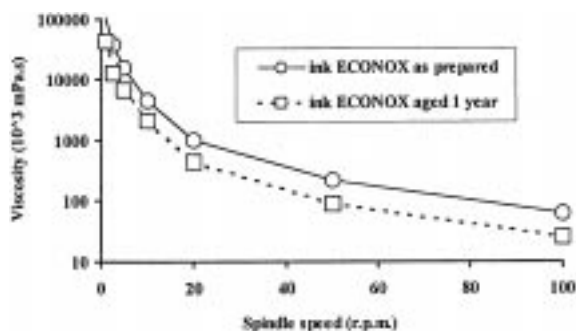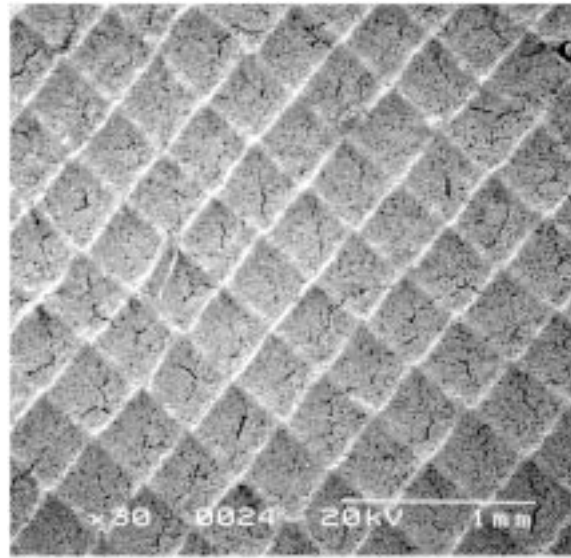

Fig. 7. Low-magnification SEM image of the thick film surface obtained by using a hand-operated machine and a low mesh number screen.

a mean thickness of about $80 \mu m$ was obtained after two consecutive depositions.

Cracks were observed on the surface of some films after firing. Their number and extension increased with film thickness, and were mainly present in hand-

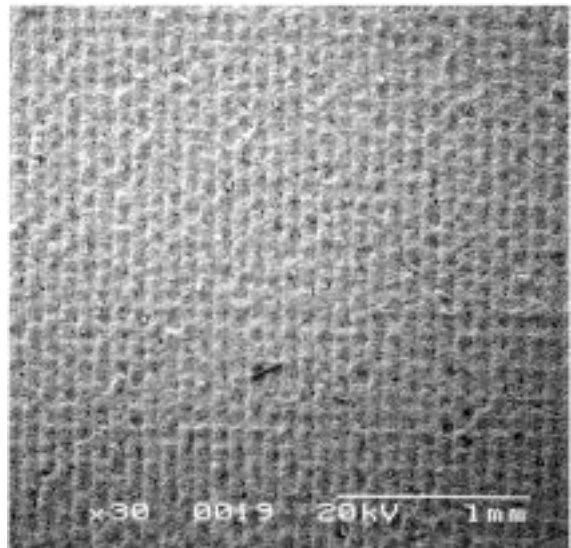Fig. 6. Viscosity changes induced by the ageing of the ECONOX ink.

Fig. 8. Low-magnification SEM image of the thick film surface obtained by using an automatic industrial machine and a 325 mesh screen.

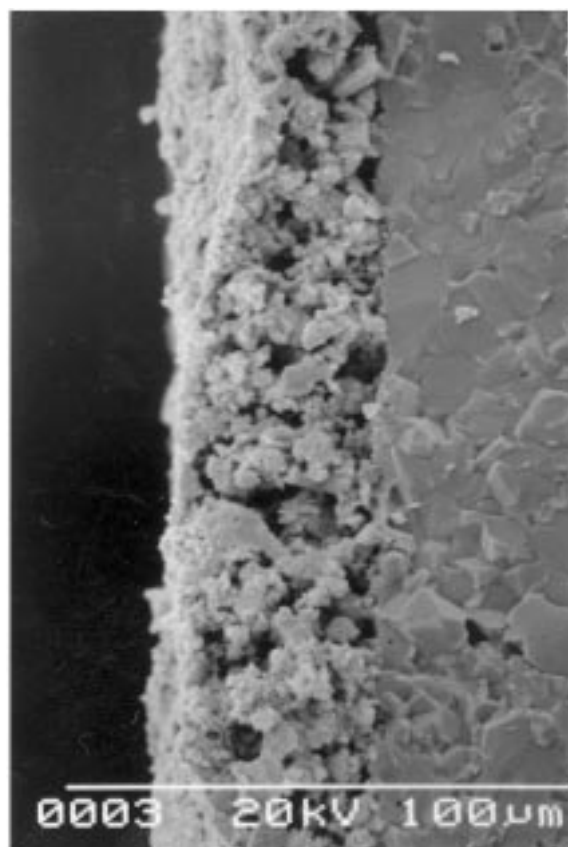Fig. 9. SEM image of the cross-section of a screen-printed film (on the right of the image, the α-alumina substrate).

Fig. 10. XRD pattern of the thick film after firing at 900°C. (β: β-alumina; N: NaAlSiO$_4$).

composition of these sodium aluminosilicates is consistent with a reaction between the glassy binder and the β-alumina: the glassy phase must be in fact enriched in sodium and aluminium oxides to yield NaAlSiO$_4$.

The emf resulting between the two metal (Au and Pt) electrodes, sputtered on the thick films, under gas injections (300 ppm CO in air at 500°C) was also measured versus time [3,8]. Limited response differences as a function of the mesh number of the screen used to print the films were detected. About 15% emf increase was observed passing from a 200 mesh film to a 400 mesh one. If cracks affected the film surface, weaker and noisy signals were recorded. Long-term stability of the signal was achieved by increasing the smoothness of the film surface, probably due to a better contact between the metal electrodes and the films. The variation in data was less for the automatically printed films than for the hand-deposited ones [8].

printed films. The cracks were probably generated during drying and extended by the shrinkage associated with firing and softening of the glassy binder.

After firing at 900°C the screen-printed inks contained a mixture of β-alumina, nepheline and carnegieite, and a residual glassy phase, as detected by XRD (Fig. 10). Nepheline and carnegieite are both sodium aluminum silicates NaAlSiO$_4$, which only differ in peak intensity ratios. Their presence should not be negative because their have an ionic conductivity $(\sigma_{300°C} = 3 - 7 \cdot 10^{-5}\,\Omega^{-1}cm^{-1})$ [9] higher than that of the glassy binder.

It was also observed that these compounds were not yielded by a spontaneous crystallization of the glassy phase during firing at 900°C. In fact, a pure glass sample, heat-treated following the same thermal cycle of the thick films, did not yield any crystalline phases, detectable by XRD (Fig. 11). In addition, the
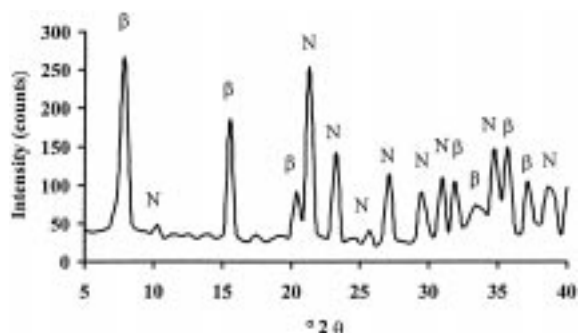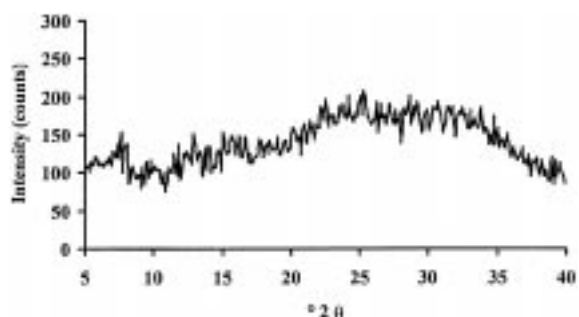

Fig. 11. XRD pattern of the glassy binder heat treated at 900°C.

4. Conclusions

The scale-up of the screen-printing of β-alumina based inks for the development of a prototype gas sensor for automotive application was followed from a hand-operated apparatus to an automatic production machine.

By lowering the mean particle size of the β-alumina/glassy binder mixture and reaching a narrow particle size distribution, it was possible to reduce the glassy phase content necessary for good adhesion of the thick film to the substrate. It was also demonstrated that new crystalline phases, nepheline and carnegieite, were given by a reaction between β-alumina and the glassy binder, during heat treatment at 900°C. These phases have a higher ionic conductivity than the glass, and their presence does not have a negative effect on the sensor response characteristics.

The viscosity characteristics of the ink were optimized by choosing appropriate organic components (liquid dispersant and rheological agent) and by optimising the inorganic/organic component ratio.

By increasing the smoothness of the films and by controlling their thickness, it was possible to improve the long-term stability of the sensing voltage, probably due to a better adhesion of the metal electrodes, and the avoidance of cracks during drying and firing. However, little difference due to mesh size was detected.

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