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Effect of Heating Cycle on the Structure of Ag Films Deposited over Porcelain Substrates

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Silver films were deposited over porcelain substrates by using flexible adhesive transfer layers. These films were produced in order to use porcelain utensils over household induction heating plates. Mixtures of different glass ceramic powders with silver powder are used to prepare the self-transfer patterns. These patterns are deposited over porcelain substrates and sintered using different heating cycles. One defect observed in such films is the presence of porosity either at the Ag/porcelain interface or inside the Ag film structure. While lower sintering temperatures produce less porosity, the microstructure of the Ag layer at lower temperatures is no longer composed of a contiguous network of large silver agglomerates. Consequently, the heating capability of the layer through electromagnetic induction is affected. Finally a sintering cycle is proposed for which the film properties are least modified with a minimum level of porosity.

Keywords Ag thick films, induction, porcelain, sintering

1. Introduction

Induction heating of food products for cooking or re-heating has become a useful and widely employed technique in recent years. The heating plate is composed of a medium frequency (20 to 45 kHz) spiral shape induction coil, continuously cooled through forced circulation of air. In such a system, the vessel containing the food is heated directly through induction currents and thus should be an electric conductor with appropriate electrical properties and dimensions. The container should be placed at some appropriate distance from the induction plate to obtain efficient heating through induced currents. This eliminates the use of traditional ceramics and glasses, which are electrical insulators.

The idea of depositing conducting films on the surface of ceramic substrates (e.g., porcelain utensils) to allow use in induction heating has recently attracted interest and resulted in a number of patents (Ref 1-5). Initially such films were produced to help in the use of ceramic utensils in microwave ovens. One such method (Ref 1, 4) was exploited to produce a heat conductive coating composed of three layers on a cooking vessel. In the conductive layer, heat was generated through induced electric current. The second layer absorbed and conducted heat energy to the porcelain substrate, and the third layer formed a protective film. A mixture of gold and silver powders with a glass powder, in an appropriate solvent, was used to produce the conductive layer. The protective layer consisted of a mixture of iron oxide and glass powder. The glass powder present in each was incorporated to accelerate the sintering operation through the formation of a low viscosity phase, to produce a good wetting between the layers, and to compensate for the differences in thermal expansion between layers during heating and cooling. Another such attempt (Ref 2) was made to deposit Ag coatings for the purpose of induction heating, but many problems such as control of film structure, form, and thickness remain to be resolved in order to control heating rate and obtain uniform heating.

In utensils made for use in microwave ovens, partial heating comes from the heat absorbed through the coating whereas the major portion of heat is produced directly inside the food. Thus the coating provides complementary heat source. On the other hand, use of conductive coatings for the induction heating of ceramic utensils can generate complex problems like nonuniform heat distribution and overheating of peripheral zones (skin effect). High temperatures are produced inside the coating due to the fact that the only heat source is the coating itself and no other external heat source is employed to supplement it. The present work is related to the development of porcelain (ceramic) utensils, which are made receptive to the induction heating. The solution to this problem resides in the use of metallic films with defined thermal and electrical properties that are constant over a life span and can generate heat due to induction in a uniform manner over porcelain surface.

These films are obtained through sintering of a mixture of silver powder and a glass powder, which forms a glaze at the surface of the porcelain. For an efficient heat transfer in the porcelain substrate, many parameters should be considered. The most important ones are the thickness and dimensions of the film, the microstructure of silver agglomerates inside the sintered glaze, and the concentration of silver in the glaze mixture. A three dimensional network of silver particles should be obtained inside the glass matrix to ensure the passage of current. This paper describes the structure to property relationship of silver films, the goal of choosing an appropriate sintering cycle.

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2. Deposition of Ag Films

A mixture of glass powder and silver powder is used to produce these films The powders are mixed together in an organic solvent to form a self-adhesive, flexible, transfer layer deposited over a backing sheet made up of a release layer and a transfer layer. The glass powder, called a flux, is mainly composed of oxides of Pb, Si, Sn and Na, with very small amount of CaO and K_2O. The presence of a flux is necessary for such an application for aesthetic, hygienic, and technical reasons. Figure 1 presents the particle size distribution of Ag powder (CERDEC 512, Cerdec Drakenfeld, Washington, PA), measured using x-ray sedigraphy techniques. The majority of the powder particles have sizes ranging from 0.1 to 1 µm. This powder is mixed with a flux (CERDEC 192001) to form a paste in a ratio of 73 wt% Ag to 27 wt% flux. This paste is added in an organic solvent (CERDEC 80612) to produce an ink. The ink thus formed is used to produce uniform thickness transfer layers composed of a backing sheet made of polyethylene-paper laminate and a water soluble release layer of $(R_2SiO)n$ type, where R is methyl or alkyl radical and n is a positive integer. The film, after sintering, shows a glassy glazed surface on cooling, with silver particles embedded as a contiguous network inside the glaze. This glaze helps achieve good contact and adhesion between the silver agglomerates and the porcelain substrate. It protects the silver particles against wear and therefore helps to increase the life of the deposited film.

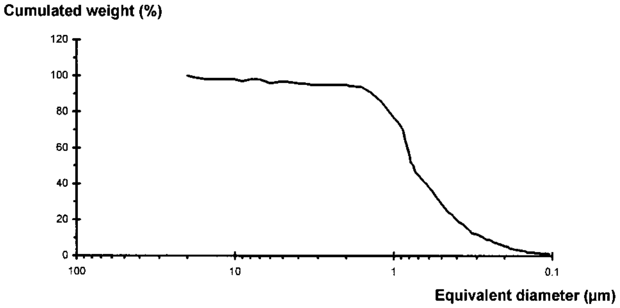

Fig. 1 Particle size distribution of the Ag powder (CERDEC 512) measured using X-ray sedigraphy technique (Sedigraph 5000 D, Micromeritics)

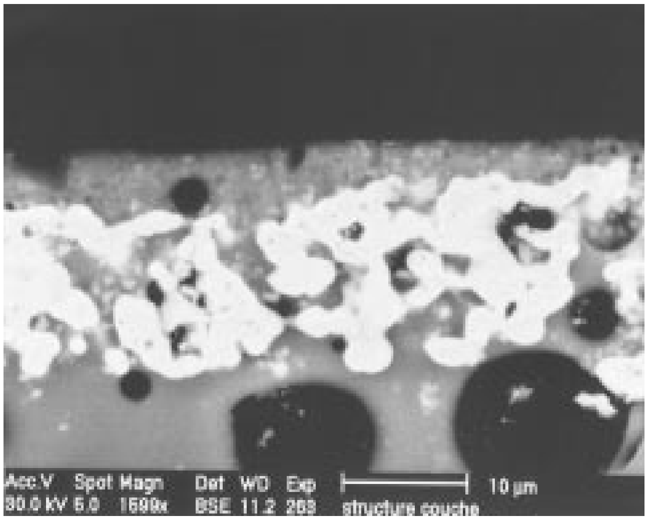

Fig. 2 Microstructure of a silver film with an initial thickness of 27 µm sintered at 820 °C

3. Microstructure and Properties of Sintered Films

A film with initial thickness of 27 µm was deposited over a porcelain disc of 5 mm thickness and 140 mm diameter, using the technique explained in the section "Deposition of Ag Films." The variation in the film thickness was measured to be ± 2 µm. Sintering was performed at 820 °C, with a dwell time of 10 min and a heating rate of 5 °C/min. Figure 2 shows the microstructure of this film. The thickness is reduced to 20 µm after sintering. This is mainly due to the densification effect and to the removal of organic components incorporated in the film during processing. The residual organic additives produce bubble like pores that can be observed in the micrograph. Formation of pores shows that the glaze becomes partially liquid at the sintering temperature. The silver particles form large agglomerates and migrate to one side of the film, probably because of differences in the density.

The film was heated over a SAUTER induction plate working at 45 kHz (2.8 kW). Temperature variation as a function of time, at different distances from the center of the film, was measured. The inductive power was kept at half of the maximum available inductive power. Figure 3 shows the distribution of temperature at different distances on the surface of the silver film. The temperature tended to stabilize between 180 and 200 °C. The temperature was attained at the periphery of the film.

The variation of electrical resistivity as a function of temperature, for two different compositions of silver films, is presented in Fig. 4. The electrical resistivity increases with temperature but the film, which is richer in silver, exhibits slightly lower resistivity at all temperatures. The self regulation of temperature at around 180 °C results from the fact that the inductive coil cannot couple to a conductor having resistance higher than a threshold value. At 180 °C, the resistance of the film attains a value such that no current can be induced in the

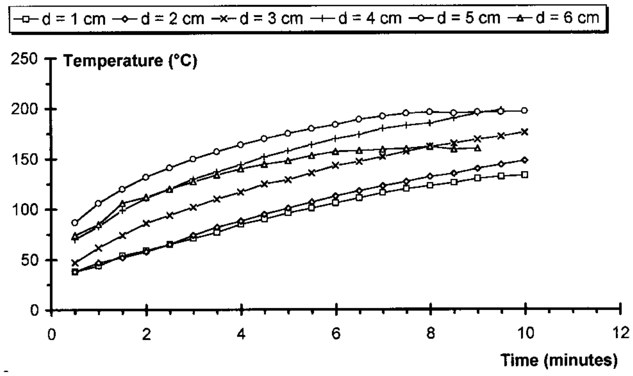

Fig. 3 Variation of temperature of a 27 µm thick silver film as a function of time, at different distances from the center of a porcelain disc, heated over an induction plate operating at 45 kHz and 1.4 kW power.

film (under the given conditions of inductor power). Thus the heating stops, and the temperature falls down. Reduction in temperature reduces the resistance and the induction heating starts again. This self regulation of temperature, which is dependent upon the resistance of the film, is an interesting and useful phenomenon.

4. Study of Sintering Cycle

In cases where thicker films were employed, the temperature rise was so rapid that it resulted in fracture. This problem was complex as it was related not only to the film properties, but also to the power of the induction coil, the thermal and thermo-mechanical properties of the substrate, and the distribution of temperature inside the substrate. Work was initiated in different laboratories (including the Laboratory of Ceramic Materials and Surface Treatments (LMCTS), University of Limoges, France; the Laboratory of Induction Technology (LRTI), University of Nantes, France; and the Laboratory of Thermal Engineering and Energetics (LGTE), University of Poitiers, France) to resolve these problems and to find a correct combination between film structure, substrate, and inductor plate. This work is related to the structure and heating cycle relationship for films of different thickness and configuration.

Glazed as well as non-glazed porcelain substrates were used to carry out these experiments. In all cases porcelain substrates with more than 95% relative density were used. The layers were sintered at different temperatures with a heating rate of 5 °C/min and the samples were kept at the sintering temperature for 10 min. Films for different thicknesses and configurations were sintered in order to find a well adapted sintering cycle.

5. Experimental Results and Discussion

A double layer configuration (each layer 27 μm thick) was initially tried. When these layers were sintered at 820 °C, large pores were observed at the interface between the two layers (Fig. 5). Porosity was also observed at the interface between the substrate and the film. The pore could be observed from outside the film via the naked eye. As the pores tend to join and grow at sintering temperatures, very large pores resulted (Fig. 6). These pores were present preferentially at the boundary between the two silver layers, rather than at the interface between the substrate and the film, perhaps due to the presence of residual organic material between the layers. The two silver layers could be easily observed as separate despite contacts at some places.

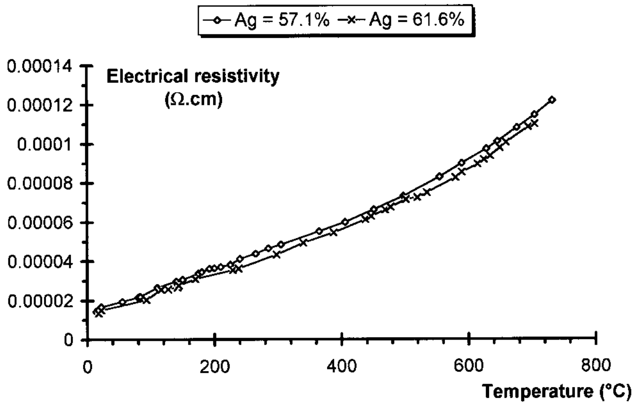

Fig. 4 Variation of electrical resistivity as a function of temperature of two silver films with different silver concentrations

In order to reduce the problem of large pores, thick single layers of 54 μm initial thickness were developed. The sintering temperature was the same (820 °C). In this case (Fig. 7) most of the porosity was present at the interface between the glaze and the substrate. The pores were slightly fewer in number than those in the earlier case but their dimensions were such that they completely modified the film texture.

Two different sintering temperatures were used (760 °C and 780 °C) with similar heating and cooling rates. In a 54 μm single layer sintered at 760 °C, almost no migration of silver particles was produced during sintering, whereas a large quantity of

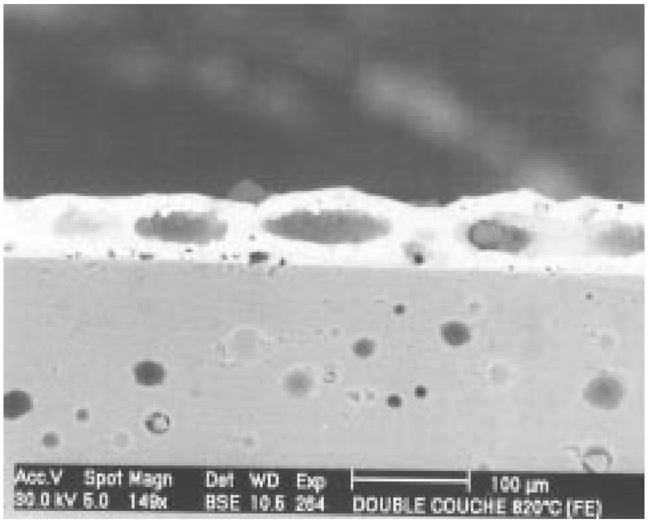

Fig. 5 Structure of a 27 × 2 μm double layer sintered at 820 °C. Large size pores can be observed between the two silver films.

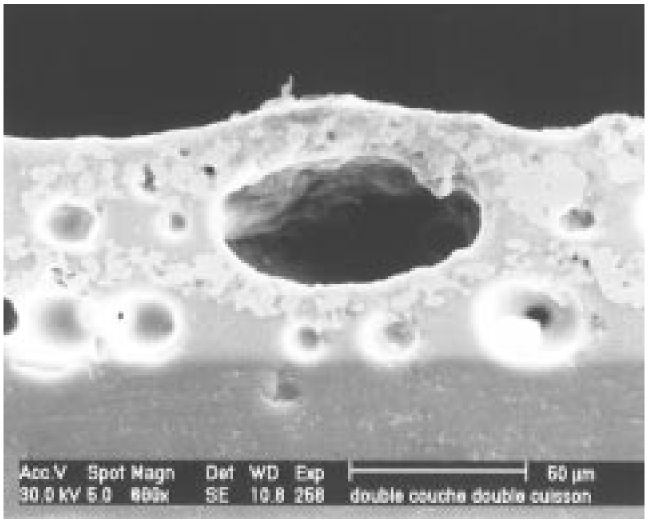

Fig. 6 Magnified vision of a pore produced at 820 °C inside a double silver layer

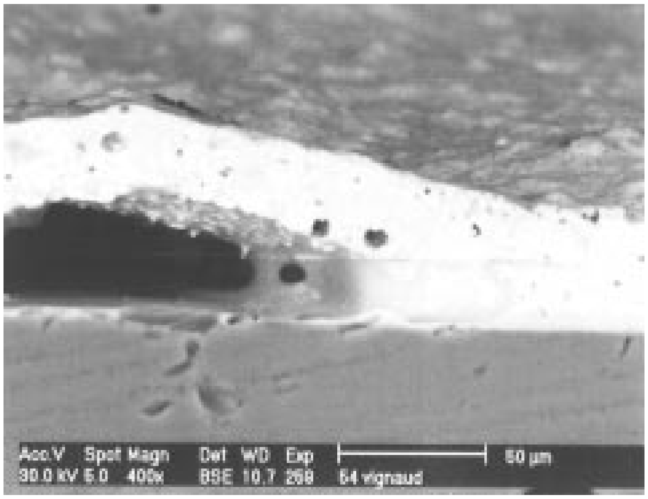

Fig. 7 In the case of a single layer of 54 µm initial thickness sintered at 810 °C, large pores were produced at the interface between the substrate and the film.

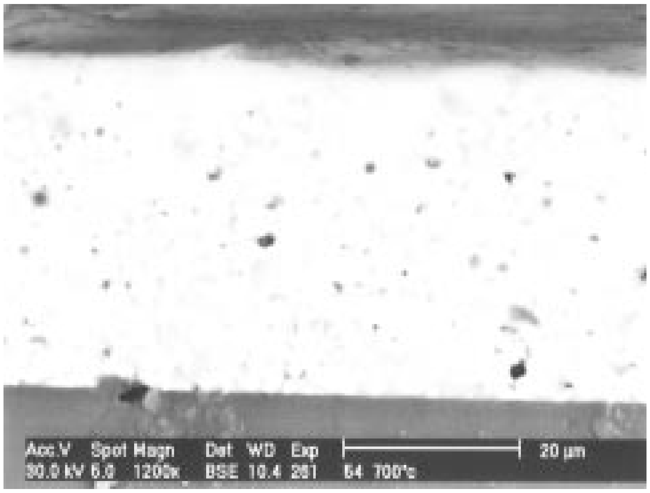

Fig. 8 Structure of a 54 µm silver film sintered at 760 °C. The fine structure of silver grains and porosity can be observed inside the film.

small pores were observed inside the film (Fig. 8). This microstructure indicated that the film was not adequately sintered. A film produced under such conditions may develop a weak adherence over the porcelain substrate. The surface appearance of the glaze indicated that the flux was not completely transformed into the glass phase at the sintering temperature. This was also a problem from an aesthetic point of view. Increasing the sintering temperature to 780 °C improved the microstructure (Fig. 9). The microstructure was very similar to the one shown in Fig. 2. The observed pore size was between 3 to 5 µm. The interface between the coating and the substrate was devoid of large pores as observed in films sintered at 810 °C. This provided improved contact between the film and substrate, with minimum porosity and better thermal shock resistance. The surface of the film appeared smooth glaring to the naked eye.

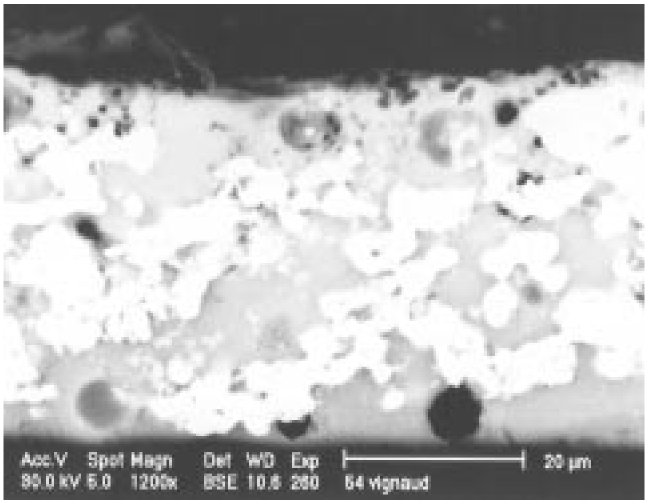

Fig. 9 SEM micrograph showing the structure of a 54 ± 2 µm silver film sintered at 780 °C

6. Conclusions

Processing conditions were established for preparing adherent silver coatings over porcelain substrates for induction heating purposes. The sintering cycle was adjusted in order to obtain a dense glaze structure with minimum porosity. During the heating process, these films have shown an interesting phenomenon of self regulation. At sintering temperatures higher than 800 °C, large size pores were produced inside films of thickness greater than approximately 50 µm. This porosity was probably attributable to the decomposition of residual organic material incorporated in the film in processing. Lower sintering temperatures resulted in less porosity but adversely modified the microstructure of the film. Finally a sintering temperature of 780 °C was found to be optimal.

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