Surface engineering glass-metal coatings designed for induction heating of ceramic components

Amir Azam Khan and Jean Claude Labbe

1Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia
2Institut Universitaire de Technologie (IUT), Université de Limoges, 87060 Limoges, France

E-mail: akamir@feng.unimas.my

Abstract. The term Surface Engineering is of relatively recent origin and use, however, the use of coatings and treatments to render surfaces of materials more suitable for certain application or environment is not new. With the advent of Vacuum Technology, Surface Engineering has gained a whole new impetus, whereby expensive materials with adequate mechanical, chemical and thermal properties are being coated or treated on their surfaces in order to achieve what is called as Surface Engineered materials. The present paper presents an overview of recent achievements in Surface Engineering and gives a detailed view of a specific application where glass-metal composite coatings were deposited on ceramic components in order to render them sensitive to induction heating. Sintered glaze coatings containing silver particles in appropriate concentration can be used for the induction heating of porcelain. Mixtures of glass ceramic powders with silver are used to prepare self-transfer patterns, which are deposited over porcelain. Several configurations of these coatings, which are aesthetic to start with, are employed and heating patterns are recorded. The microstructure of these coatings is discussed in relation to the heating ability by a classical household induction system. The results show that this technique is practical and commercially viable.

1. Introduction

Materials surfaces can be modified at the atomic, micro and macro level in order to obtain, what is called as Surface Engineered materials. This modification can be brought about through Surface Treatment or Surface Deposition process. In each case, surface properties are engineered in a way to obtain specific properties which would otherwise be impossible if only bulk materials are employed. The earliest use of Surface Engineering can be traced back to the Egyptians some 5000 years ago. The use of ink for writing can be considered as the oldest form of surface engineering.

During the last 40 years or so, Surface Engineering has emerged as an avant garde of Materials Engineering and Processing. Novel materials are deposited on substrates through techniques which make use of vacuum or inert environment. This provides solution to engineering problems for severe or demanding applications. The surface modified components are in some cases cost effective and in other cases only available options for specific applications. Examples can be such as Thermal Barrier Coatings (TBCs) on turbine blades [1,2] and zirconia coatings for wear resistance and corrosion protection [3].

An almost unlimited range of processes is available but the choice of a process depends on several parameters such as size of the component, structure of the coating, process cost, deposition rate,
environment, pressure, temperature and working conditions etc. For electronic and optical applications, atomic/molecular layer deposition processes such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) for example, are used. Very thin wear resistant coatings can also be obtained using the same techniques. For thick wear resistant coatings for corrosion, wear or thermal protection, a range of thermal spraying techniques can be employed such as High Velocity Oxy Acetylene (HVOF) spraying, Thermal Plasma Spraying (APS, LPPS, TPS), Thermal Arc Spraying and Detonation Gun Spraying. Chemical and/or Electrochemical routes can be employed through Electrodeposition, Electroless Deposition, Paints, Galvanizing, etc.

The present work discusses the application of Surface Engineering in the domain of decorative coatings. These coatings have been used in the form of glaze on porcelain for several hundred years. Glazed glass panels can be found on the windows of ancient buildings in Europe and Asia, some dating back to more than 1000 years. A glaze is a glass coating applied in the form of a glass powder. A heating process converts this fine powder attached to a surface into a molten glass film of a given color. Upon solidification this film converts to a reflecting colored glass which provides several advantages in addition to give an aesthetic value. Glazed surfaces don’t absorb water hence can be cleaned easily. Glazed film is composed of a mineral glass which is relatively inert to the environment, hence the life of the substrate is increased. The glazed coatings can also be used for the heating purpose. The Induction heating of food products, for cooking or re-heating purpose, has become a useful and widely employed technique in the recent years. The induction heating is done using a medium frequency (20 to 45 kHz) spiral shaped induction coil, continuously cooled through forced circulation of air. In such type of system, the vessel containing the food is directly heated through induction currents and therefore, should be an electric conductor with appropriate electrical properties and dimensions. It should be placed at some appropriate distance from the induction plate in order to obtain efficient heating through induced currents.

The idea of depositing conducting films on the surface of ceramic substrates (e.g. porcelain utensils), in order to allow their possible use through induction heating, has recently developed a lot of interest and has also resulted in the demand of a number of patents[ 4,5,6,7,8]. Initially this type of films was developed to help in the use of ceramic utensils in microwave ovens. One such attempt was made to deposit silver coatings for the purpose of induction heating. Many problems such as control of film structure, form and thickness remain to be resolved in order to control heating rate, to obtain required temperatures and to eliminate the risk of fracture in porcelain through rapid heating. Some work has been conducted and published on mixtures of glaze with silver particles, sintered together to produce silver containing glazes [ 9, 10]. Further study on combinations of continuous and discontinuous glazed layers of different thickness is presented in the following work. The objective is to obtain as much as possible, a uniform temperature distribution on the surface of the plate, making it safe for use under induction heating.

2. Experimental Results and Discussion
A mixture of glass powder and silver powder is used to produce these films. They 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 as flux, is mainly composed of oxides of Pb, Si, Sn and Na, with small amounts of CaO and K₂O. The presence of a flux is necessary for such an application due to aesthetic, hygienic and technical reasons as it transforms to a glaze after sintering. Figure 1 presents the particle size distribution of Ag powder (CERDEC 512 origin Matthey Beyrand, France), measured at the laboratory using X-ray sedigraphy. It can be seen on this figure that majority of the powder particles have sizes ranging between 0.1 to 1 µm. This powder is mixed with a flux (CERDEC 192001 origin Matthey Beyrand, France) to form a paste, in a ratio of 73 weight % Ag – 27 weight % flux. this paste is added in an organic solvent (CERDEC 80612 origin Matthey Beyrand, France) to produce an ink, which is used to produce uniform thickness transfer layers. The overall percentage of Ag, including the flux and solvent comes out to be 57.1 %. The film, after sintering, shows a glassy glazed surface on cooling, with silver particles embedded as a contiguous
network inside the glaze. This glaze also helps to accomplish a good contact and adhesion between the silver agglomerates and the porcelain substrate. It protects these particles against wear and therefore helps to increase the life of the deposited film.

The heating plate is constituted of a magnetic induction coil working at medium frequency between 20 and 45 kHz. The transferred film after sintering at around 820 °C on the plate surface gives a thickness of 27 +/- 2 µm but due to segregation of Ag particles the zone containing Ag agglomerates is about 15 +/- 3 µm thick. Figure 2 presents the microstructure of this film. On the same figure it can also be seen that the glassy phase produced by the melting of the flux contains spherical pores. These pores are a typical feature of a glaze on porcelain. Major effort is required to keep these pores as little as possible in number and size to give a good thermal conduction between the deposited layer and the porcelain substrate. This is mainly due to the densification effect and due to the removal of organic components incorporated in the film during processing. The presence of bubble like pores shows that the glaze becomes partially liquid at the sintering temperature. The silver particles form large size agglomerates and migrate to one side of the film, probably due to differences in the density. It should be noted that on the micrograph it appears that the Ag particles/agglomerates are not in contact at some points, but as the film is in three dimensions whereas the micrograph gives a 2 dimensional view, this impression can be misleading.

These initially deposited films were tested on the induction plate for their heating performance. The porcelain plate was of 140 mm diameter and 5 mm thickness. It was placed on the induction plate in such a way that the film was facing upwards. This gives a coupling distance between the film and induction coil of the same order as to a distance between heating coil and film as used under real conditions (about 11 mm). The plate is heated and temperatures at the surface are measured using thermocouples attached at equal distances. The Figure 3 gives the result of temperature variation as a function of time at different distances from the center of the plate.

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

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As it can be seen on Figure 3, for a film of 27 +/− 2 µm thickness heated at half power, the temperature stabilizes at about 200 ºC at a distance of about 5 cm from the center of the plate. The temperature remains lower at all other points on the surface of the plate. Two important observations are worth noting. The highest temperature is not located at the center of the plate, nor at its edges, but at a distance of 5 cm from the center. Secondly, there is an auto-regulation of temperature, which takes place due to coupling-decoupling of the induction coil with the silver film. It is expected that this would change as the thickness of the film or the induction frequency would change.

2.1 Structure of silver coatings at different thickness and sintering temperature

The simple continuous film with a thickness of 27 +/− 2 µm creates a heating pattern which can give a damaging thermal shock in case the plate is heated without any food in it. It was found that sudden heating of the film can create cracks. Several options were negotiated to reduce this thermal shock. The shape and thickness of the film were manipulated in order to reduce the temperature gradient over the surface of the porcelain. 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 ºC.min⁻¹ and the
samples were kept at the sintering temperature for 10 minutes. Films of different thickness and configurations were sintered in order to find a suitable sintering cycle. The Figure 4 shows the microstructure of a 54 \pm 2 \mu m film. The sintering was carried out at 760 °C. This temperature is barely enough to sinter the glass powder. This gives an advantage that there are no large size pores and the silver particles are not agglomerated as they are in the sample shown in Figure 2. The sample in Figure 2, sintered at 820 °C, contains large size pores due to degassing of solvent at high temperature and silver particles migrate and agglomerate under gravity and under long range surface forces. On first sight this microstructure seems acceptable, but this coating can degrade over time very quickly as glaze is not entirely sintered and attached to the porcelain surface. Moreover, further sintering and shrinkage of the film is possible while heating over induction plate.

![Figure 4](image4.png)

**Figure 4.** Structure of a 54 ± 2 \mu m silver film, sintered at 760 °C. The fine structure of silver grains and porosity can be observed inside the film.

![Figure 5](image5.png)

**Figure 5.** SEM micrograph showing the structure of a 54 ± 2 \mu m silver film, sintered at 780 °C.

Figure 5 presents the microstructure same film sintered at 780 °C. The difference in microstructure is visible in this micrograph. The silver particles are agglomerated relative to the previous one and there is presence of pores, although these are not of very large size. From point of view of optimization in sintering cycle, this cycle seems to fulfill and optimize the properties of the film.

### 2.2 Design of silver coatings

Once the sintering and microstructure of the film is optimized, the second stage is to design the film in a manner so as to distribute the temperature as evenly possible. This would create a condition for lowering the thermal shock. Several configurations were investigated, three of them are shown in Figures 6, 7 and 8.
The Figure 6 (a) presents a modified design in which a discontinuous layer in two halves is deposited. The layer thickness is 27 ± 2 µm at the time of deposition. The Figure 6 (b) shows the temperature distribution on the surface of porcelain substrate under similar conditions as mentioned under section 1. The areas close to the centre of the substrate now reach higher temperature which is better than the previous continuous layer, but the maximum temperature has dropped from approx. 200 °C to 120 °C. Other configurations are also tried as shown in Figures 7 and 8. By increasing the number of discontinuities within the film, the temperature distribution over the surface is improved but the maximum temperature drops for each discontinuity. The temperature reaches mere 35 °C in the case of a film with 4 discontinuities.

The objective of this exercise is to introduce within a conducting layer, non-conducting zones so that the current flow trajectory can be changed. As it can be seen, this helps to change the heating pattern.
towards a more regular one, but greatly reduces the heating efficiency. As a general statement we can
say that any tentative to bring the current more towards the centre of the substrate would reduce the
current intensity, resulting in lower efficiency. The solution is more complex than initially envisaged.
The solution lies probably in combining the effect of discontinuities of the film, to improve
temperature distribution and increasing the thickness of the film. As shown in previous section
(Figures 4 and 5) films of greater thickness can be transferred to the porcelain substrate and sintered
successfully. This thing has to be taken with care, as increasing thickness of silver coating increases
the cost as well as it is not so good from the aesthetic purpose. Some initial results were obtained for a
different design of the film.

![Figure 9](image9.png)

**Figure 9.** Temperature distribution profile measured along the diameter of a porcelain plate,
measured after 6 minutes of heating. Inner coating diameter = 105 mm, thickness 54 ± 2 µm,
outer crown between 106 to 140 mm, thickness 36 ± 2 µm.

![Figure 8](image8.png)

**Figure 8.** (a) Presents the design of glazed layer with four cuts, within a 27 µm thick
layer, (b) shows the temperature distribution on the surface of the porcelain plate.
2.3 Double layer Configuration

A double layer pattern was investigated. It composed of an inner film of $54 \pm 2 \mu m$ thickness and a diameter of 105 mm and an outer film of inner diameter 106 mm and outer diameter 140 mm. The outer layer thicknesses tried in this case is $36 \pm 2 \mu m$. In this design the inner layer ensures the central part of the substrate to remain hot. As the inner film thickness is $54 \pm 2 \mu m$, this is also expected to produce sufficient heat for the central part. The outer layer which is less thick ($36 \pm 2 \mu m$) heats the outside boundary of the substrate. Excellent results are obtained with this configuration, as shown in Figure 9. These results are obtained using an infrared camera (Hughes Inc) after six minutes of heating at half power. This figure shows the temperature distribution over a double layer combination of $54 \pm 2 \mu m$ thickness inner film and a $36 \pm 2 \mu m$ thickness outer film. It shows that the temperature is well distributed over the surface with a maximum of $150 \degree C$ situated at about 15 mm from the edge. Continued heating checks have ensured that no plate gets cracked, no matter what type of heating is conducted.

3. Conclusion

This work was conducted with an objective to study the induction heating of porcelain substrates and to improve the existing configuration of a single glazed silver layer containing no pattern. The coating microstructure and sintering conditions were also optimized and a suitable sintering cycle was proposed for which the coating exhibits minimum defects and a uniform distribution of silver particles within the glaze. The initial design was based on a continuous silver/glaze film deposited over the substrate. The heating pattern for this continuous layer gave uneven heating of the periphery of the film, with very little heat at the centre of the plate, a characteristic of induction currents. This produced a thermal shock which was damaging for the plate if it was heated empty. Initially an effort was done to use perforated or discontinuous layers in order to achieve better heat distribution but this also resulted in the lowering of the heating efficiency.

The maximum temperature obtained was significantly reduced depending on the pattern used. To further solve the problem two distinct layers of different thickness were employed. The coating was split in two parts, an inner coating of 105 mm diameter, with a slot in between, and an outer crown of 106 mm inner diameter and 140 mm outer diameter. The inner coating thickness was increased to $54 \pm 2 \mu m$ as no coupling effect was possible for a $27 \pm 2 \mu m$ film. The outer coating had a thickness of $36 \pm 2 \mu m$. By using two films of different thickness it was made possible to regulate the heating rate and to make the temperature distribution more uniform. The results hence obtained have shown that the heat remains relatively uniform. No sample showed any damage despite several heating cycles, empty or full of food.

4. References

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