Further Developments in the 3D Printing of Self-Glazing Single Fire Ceramic Materials

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Abstract

David Huson and Katie Vaughan at the Centre for Fine Print Research at the University of the West of England are continuing their research into the 3D printing of ceramic bodies by investigating the possibilities of using techniques developed by the ancient Egyptians to produce a 3D printed ceramic body that will glaze itself during a single firing process.

The Centre for Fine Print Research at the University of the West of England has funding from the Arts and Humanities Research Council for a three year research project entitled "Can Egyptian Paste Techniques (Faience) be used for 3D printed, Solid Free-form Fabrication of Ceramics?"

Now in the second year of the project this research aims to create a set of functional ceramic materials through a process based upon historic Egyptian Faience techniques, which will allow ceramic artists, designers and craftspeople to 3D print actual objects in a familiar material that can be glazed and vitrified in one firing; a breakthrough for ceramic design and manufacture.

The two methods used in ancient Egypt to enable self-glazing in one firing are efflorescence glazing and cementation glazing:

In efflorescence glazing soluble salts are introduced in to the body mix, after forming and during the drying stage these salts migrate to the surface of the formed article and during firing fuse and react with the body materials to form a glaze on the surface, by introducing colouring oxides such as cobalt, iron, manganese or copper into the mix a range of coloured glazes can be produced.

In cementation glazing the article that has been formed is surrounded in a saggar (a refractory box used to support and protect a ceramic object during firing) by a powder consisting of a glaze precursor, during the firing process a reaction takes place between the ceramic article and the glaze precursor powder and a glaze is formed on to the surface of the ceramic article, the firing temperature is below the melting temperature of the glazing powder so that the glazed ceramic article can be removed from the powder bed in which it was fired.

This is a new area of research to create a functional 3D printed real ceramic material through a process based upon historic Egyptian Faience techniques, which will allow ceramic artists,

designers and craftspeople to 3D print objects in a familiar material that can be glazed and vitrified in one low temperature energy efficient firing process, a breakthrough for ceramic design and manufacture which will be applicable to the arts and wider industries.

Introduction:

The Centre for Fine Print Research has over five years continuous experience in the 3D printing of ceramic materials for artists, designers and the ceramic industry. This particular research project aims to create a set of functional ceramic 3D printable materials through a process based upon the historic Egyptian Faience techniques, which will allow ceramic artists, designers and craftspeople to 3D print directly from a 3D CAD file an actual object in a ceramic material that can be glazed and vitrified in one firing; a breakthrough for ceramic design and manufacture.

Historical Background:

The inspiration and background research for this project is based upon Egyptian Faience. "Faience was the first glazed ceramic material invented by man."[1], Egyptian Faience is a silica based, glazed ceramic first produced in Egypt and the Near East around the 4th millennia BC The composition is based on a powdered quartz or sand body, containing traces of lime and an alkali obtained from natron or plant ash. The body was coated in a soda-lime-silica glaze that was most commonly bright blue-green in colour due to the addition of copper [2]. The main advantage of Faience was that it could be glazed, something that was not done to clay pottery until Roman times. [3]

The Egyptians referred to Faience as 'tjehnet', meaning that which is brilliant and scintillating like the sun, moon and stars [3] To the ancient Egyptians, the sun was a symbol of resurrection, and its link to Faience explains why this material was used to create funerary figurines (shabti) to accompany the dead. The turquoise blue colour associated with the earliest Faience is also thought to be symbolic of rebirth and fertility. [4]

Figure 1. Egyptian Faience Shabti British Museum

Glazing techniques:

It is now generally accepted that Egyptian Faience was glazed using three techniques; efflorescence, direct application and cementation. These techniques are not mutually exclusive and could have been in combination to produce a single object. Efflorescent glazing is a self-glazing technique that occurs when soluble salts mixed in with the body migrate to the surface upon drying to form a crust on the outer surface. Upon firing, the 'efflorescent layer' melts to form a glaze.

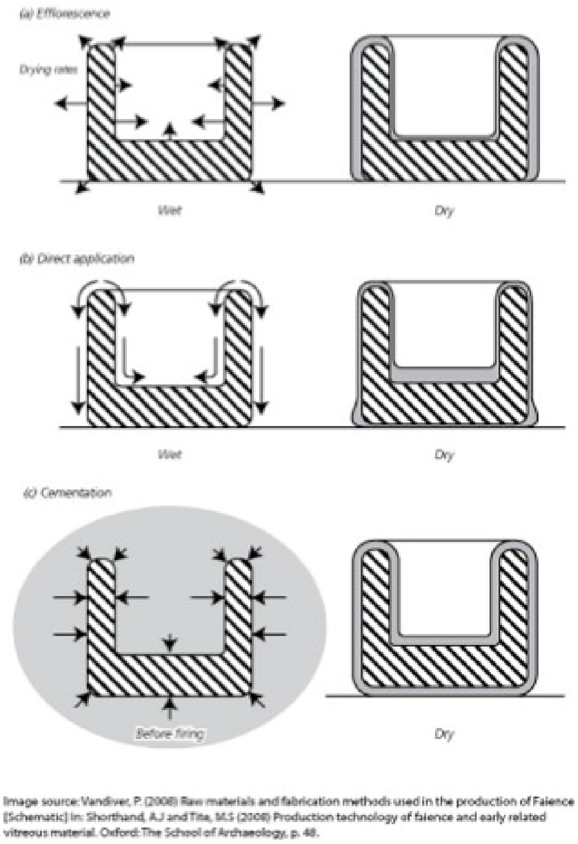

Figure 2 Egyptian Faience glazing techniques

The second glazing method used by the ancient Egyptians was application glazing. Similar to techniques used by potters today, this method involves coating the Faience object in a paste or slurry. The slurry was composed of alkalis derived from plant ash or natron and copper compounds such as malachite, which was applied to a fired object by dipping, pouring or brushing the slurry onto the body. [7] When fired the slurry melts to form a glaze on the surface of the object.

Cementation glazing is the third self-glazing technique that was first discovered and used by the Ancient Egyptians. Examples of what is believed to be objects produced by the cementation method date back the Middle Kingdom. This technique was mainly used to produce small items such as typically beads or amulets.

Research into the field of self-glazing by the cementation method has been limited. One of the most significant studies was conducted by Hans E. Wulff et al. in 1968, who gained access to a Faience workshop in Qom (Iran) where cementation glazing was still being used. Wulff witnessed the main stages of the process, from initial material preparation to the production of the final object. Wulff was allowed to take photographs documenting the process and was also given a large sample of the glaze powder and several finished artefacts to take away with him to study. The glaze powder was analysed and the ingredients and their proportions published in his paper '*Egyptian Faience – A Possible Survival in Iran*'[5], along with a replication study. It seems likely that the materials and processes used in Qom were very similar to that used in ancient Egypt, Based on Wulffs' observations, the cementation process used in Qom is detailed as follows.

"Desired objects were formed from a body composed mainly of silica. The source of silica came from carefully selected quartz pebbles that were processed into a fine powder, first using a sledgehammer and later a hand mill. The silica was then mixed with water and a binding agent to produce a paste/sticky dough that was then either hand formed into small bead sized balls, or pushed into moulds. Once dry the object was then placed in a saggar (a ceramic container) and surrounded by a specially formulated glaze power. The glaze powder was composed of a mixture of silica, soluble salts, calcium and copper compounds. During the firing process a series of chemical reactions occur, resulting in the formation of a glaze on the outer edges of the object only. Once cooled, the glaze powder is transformed into a friable mass that can be crumbled away easily to reveal the glazed object inside."

A replication study conducted by M.Matin et al [6] revealed that for cementation glazing, the glazing of faience objects is carried out by two different glazing mechanisms, namely the interface glazing mechanism (IGM) and the chloride glazing mechanism (CGM).

The IGM mechanism involves the diffusion and migration of alkali salts from the glazing powder to the siliceous faience body and the subsequent interactions that take place. A glass phase forms on the object surface to produce a glaze layer and alkali salt penetration to the object body results in the formation of a buffer layer and inter-particle glass (between the grains of silica). As its name suggests, this mechanism operates exclusively at the interfaces, so its occurrence depends on the direct contact between the glazing powder and the surface of the siliceous object.

This CGM mechanism is fundamentally a type of vapour glazing (similar to the traditional salt glazing process), based on the vapourisation of alkali chlorides. In actual practice, a combination of both the IGM and CGM glaze mechanisms are required for the successful glazing of copper blue faience objects.

In the cementation method, diffusion and migration of silica from the object to the glaze powder results in the formation of a capsule around the object. It is this capsule that prevents the glaze powder from adhering to the molten glaze forming on the object surface during the firing. It therefore plays a crucial role in successful cementation glazing and shall now be discussed further.

Compounds of calcium commonly used in ceramic production are refractory materials i.e. they have a high melting point. In the presence of silica however, calcium can act as a flux depending on its content in the mixture. In the aforementioned replication study conducted by Matin et al. [6] glazing mixtures with a SiO_2 /CaO ratio of around 1:2 were produced. In their findings they stated that "Generally the melting points of cementation glazing mixtures with such ratios are too high for producing dense sintered mixtures at about 1000°C. However by reducing the SiO_2 /CaO ratio to a value lower than 1 (1 :> 1) a dense sintered material will be obtained in actual practice." In other words, the increased amount of silica present in the glazing mixture as a result of SiO_2 migration (from the body to the glaze mixture) leads to a significant reduction in the melting point of the glazing mixture and hence in the formation a capsule. The remaining glaze mixture that has not had the SiO_2 /CaO ratio altered, does not transform into a dense sintered mass once fired and remains friable so can be crumbled away easily to reveal first the capsule and then the glazed object contained within.

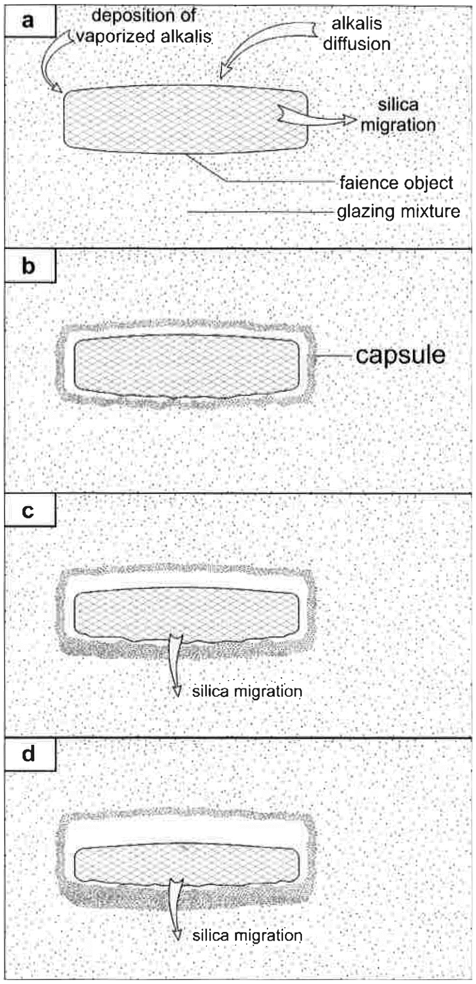

Figure 3: Diagram showing silica migration from the object to the surrounding glaze mixture during the firing process [M.Matin et al 2011]

The potential advantages of using the cementation technique are, one firing required to produce a vitrified and glazed object, the object is supported during the firing by the glaze powder meaning that there is potential for creating shapes with delicate features such as overhangs or thin sections. Theoretically, cementation glazing results in objects that are coated with an even layer of glaze with no firing marks visible due to the absence of props in both the drying and firing stages and that large numbers can be fired and glazed at one time, limited only by the size of the saggar.

The Project:

True Egyptian Faience is notoriously difficult to work with, the low plasticity of the Faience bodies makes it a very difficult material shape, if too little water is added, the material will not bend and tends to break when forming objects and if too much water is added the material becomes sticky and has a tendency to slump under its own weight. The possibility of 3D printing this type of material offers the opportunity of opening up the area of self-glazing ceramics to artists and craftspeople, the intention of the project to offer low cost routes and methods to accessing 3D technologies will benefit all interested in this fascinating material.

Efflorescence Glazing:

During the second year of the project work has involved the development of a 3D printable ceramic body containing soluble salts that will effloresce upon drying to form a glazed surface when fired. The 3D printers used for this project are the Z Corporation model Z310 powder/binder printers. In the CFPR UWE 3D printed ceramic process the standard Z Corporation plaster based powder material is replaced by a specially developed ceramic body that is activated by jetting the standard Z Corporation ZB60 binder onto the build bed to form the model layer by layer. The conventional efflorescence glazing material chosen from the trials conducted during the first year of the project was re-formulated to use the calcined alumino-silicate materials and organic binders developed during the previous CFPR UWE 3D ceramic printing projects. This has been a difficult balancing act to accomplish, as the requirements of a 3D printable material are in many ways incompatible with the requirements of a self-glazing ceramic body. To get a sufficient amount of water via the binder into the faience body mix to generate the soluble salt transfer to the surface during drying can cause layer shifting during printing and careful control of the binder saturation levels is necessary, but it has proved possible to successfully 3D print an Egyptian Faience ceramic body.

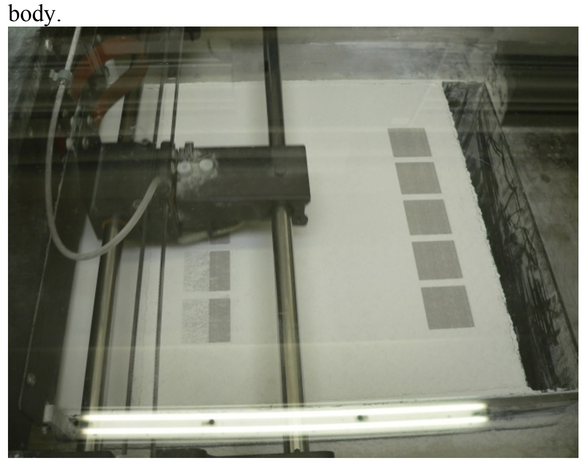

Figure 4. 3D printing Egyptian Faience body

By adding to this 3D printing Egyptian faience body a 50/50 mixture of a sodium carbonate and sodium bicarbonate, containing finely ground manganese dioxide stain it has proved possible by increasing the liquid binder saturation level to 3D print sample tiles of Egyptian Faience body which can be removed safely from the build bed and which effloresce on drying.

When fired to 950 deg. C a black glaze surface is developed on the outside of the tile due to the migration of the salts and the stain.

Figure 5. Efflorescence glazed 3D printed tile

Figure 6. Section showing glaze surface

Figure 7. 3D printed Faience necklace

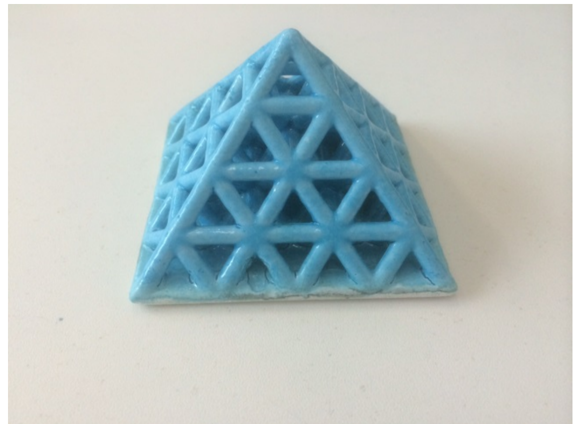

Figure 8. 3D printed Faience pyramid

Figure 9. 3D printed Faience scarab

During the course of the second year of the project this technique has been refined and developed to incorporate a wider range of colouring oxides and stains and a number of objects have been 3D printed and fired using this process.

While development into the body recipes and colour palette and the 3D printing process and parameters are still ongoing the work to date has shown that 3D printing efflorescent self-glazing materials is a viable and valuable ceramics process.

Cementation Glazing:

As the description of the cementation glazing process above indicates this is a complicated and not completely understood process. A long series of trials have been conducted to develop a silica based body that can be successfully 3D printed along with a range of glazing powders that possess the correct chemistry to develop a glaze on the surface of the bodies. Various colouring oxides and commercial stains have been used to generate a varied colour palette. Examples of some of these trials are shown below all using a base powder mix recipe of Silica 24%, Calcium Carbonate 36%, Sodium Carbonate 36% and Sodium Chloride 4%.

All trials were fired in a saggar at 950 deg C.

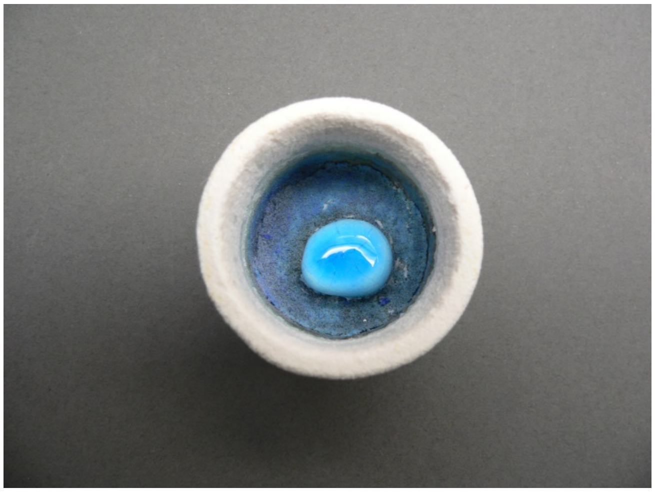

Figure 10. With 5% Copper Carbonate

Figure 11. With 5.9% Chromium Oxide

Figure 12. Stained body with no glaze stain addition

All of these trials show the capsule development caused by the migration of silica into the glaze powder and the diffusion of alkalis from the glaze powder. Figure 12 is particularly interesting ad the stains are in the body and not in the glaze powder and a clear glaze has formed on the body.

Summary:

This is the second year of a three year project to investigate 3D printed self-glazing ceramics and work to date has demonstrated the viability of applying ancient Egyptian glazing techniques to modern 3D printing technologies to develop a new type of ceramic material which has great potential for ceramic artists, designers and craftspeople as well as in the field of ceramic education. Trials on the cementation glazing process are proceeding well and 3D printable bodies and forms are being developed for this particular process. During the final year of the project it is envisaged that there will be a series of workshops and a symposium that will be held will be held to disseminate the results of the project. Artists will be invited to submit 3D files to be produced.

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Author Biography:

David Huson is a Senior Research Fellow in the Centre for Fine Print Research at the University of the West of England in Bristol.

Having worked for over 25 years in the U.K. ceramic industry, he is currently researching 3D printed ceramics, photo ceramics and the use of digital fabrication techniques for Art/Crafts, Designer/Maker ceramics and industrial applications. In 2011he was awarded the Saxby medal by the Royal Photographic Society for his work on 3D imaging.