3D printed self–glazing ceramics: process and materials development

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Abstract

David Huson and Katie Vaughan David Huson and colleagues 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 final 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 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 paper will describe the development of a 3D printable ceramic body with a glaze precursor powder for the cementation glazing process. (the initial development work was described in a paper presented at DF2014) The process parameters, formulations and 3D printing settings required will be detailed and images and examples of artefacts made by this process will be included. 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 and designers to 3D print objects in a material that can be glazed and vitrified in one low temperature energy efficient firing process, a potential 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][4[, 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]

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.

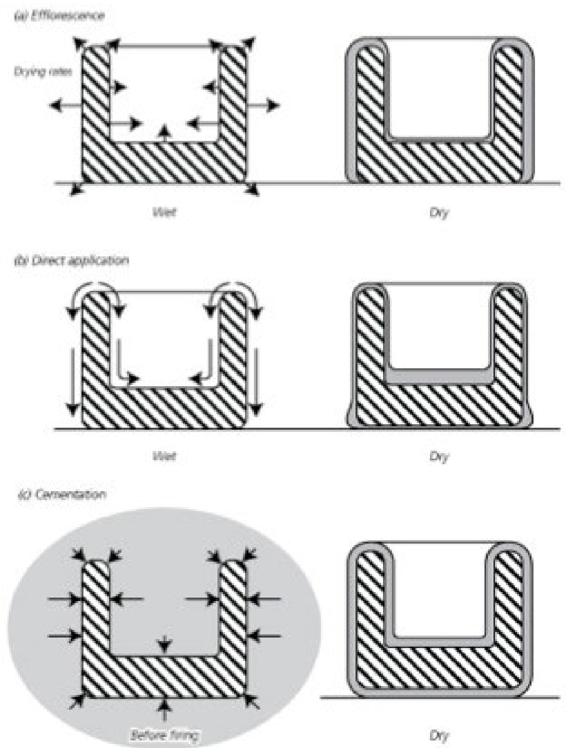

Image source: Vandiver, P. (2008) Raw materials and fabrication methods used in the production of Faience [Schematic] In: Shorthand, A.J and Tite, M.S (2008) Production technology of faience and early related vitreous material. Oxford: The School of Archaeology, p. 48.

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 [5]. 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.

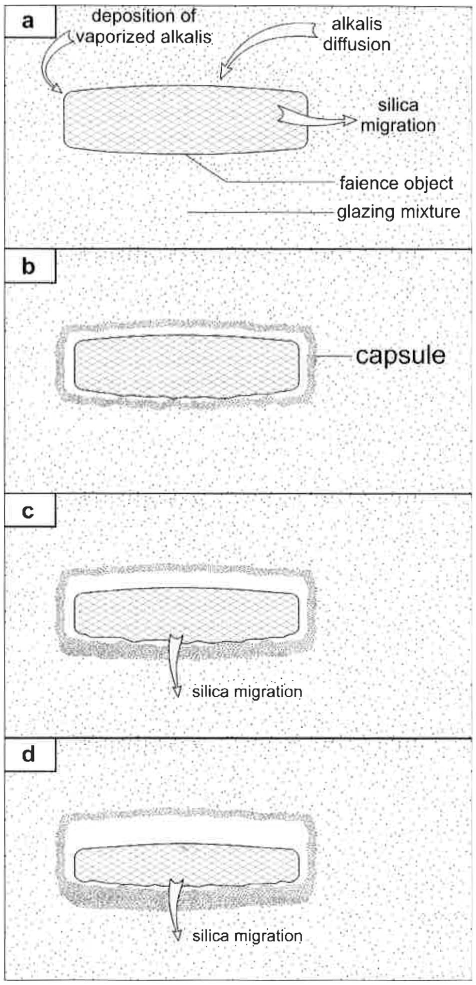

Figure 3: Diagram showing silica migration from the object to the surrounding glaze mixture during the firing process [M.Matin et al 2011]

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.

Cementation Glazing:

As the description of the cementation glazing process above indicates this is a complicated and not yet completely understood process. A 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.
The following trials were conducted to refine the glazing process and to optimize the 3D printable body material.

Trial 1:

This trial was conducted by using a glaze mix, 1a containing the following:

Sodium carbonate 35.3 %
Calcium carbonate 35.3 %
Flint 23.5 %
Copper carbonate 5.9 %

This glaze recipe was dry ball milled for 8 hrs to ensure a homogeneous mixture. Three different 3D printable body mixes were created to test the glazing process:

BR1 Fused silica 100%
BR2 Flint 100%
BR3 Fused silica 50% Flint 50%

Objects made from body recipe BR1,BR2 and BR3 were buried in glazing mixture 1a in a saggar and fired in an electric kiln for 10hrs to 1000°C, with a 20 minute soak.

Figure 41: body test pieces (Left BR3, Middle BR2, Right BR1)

Observations:

Patches of glaze and colour have been formed on the surface of all three objects.
The glaze material would benefit from being made to be more porous and friable as significant force was required to remove these objects that has resulted in breakages of two of the test pieces.
The glaze powder has adhered to all three objects. This is most extreme in the case of the flint sample (left), where the object fused completely to the powder surrounding it. The fused silica sample (right) adhered to the glaze mixture least out of the three samples.
The body strength was not strong enough to withstand removal from the glaze powder. However, the extent of powder adhesion (especially on the flint sample) makes this an unfair criterion to use for this particular trial.
The partial glazing the all three test pieces using this glaze powder recipe demonstrates that the cementation glazing technique is working in part. The extensive replication study conducted by M.matin et al [6] describes two glazing mechanisms that work in combination with one another in the cementation method. This trial demonstrates the patchy glaze and colour that one might expect as a result of the interface glazing mechanism (IGM). The IGM involves the diffusion and migration of alkali salts from the glazing powder to the siliceous faience body and the subsequent interactions that take place to form a glaze on the surface. As its name suggests, this mechanism operates exclusively at the interface between glaze powder and body surface. Characteristics of the IGM include a thin glaze coating that is typically whitish blue, with pale blue/ blue patches. The test pieces produced in this trial are indeed coated with a thin white glaze with blue patches.

The chloride glazing mechanism (CGM) is the second mechanism that features in successful cementation glazing. The CGM requires the presence of alkali chlorides in the glazing mixture and involves the deposition of glaze and colour on the object by vaporisation of copper and alkali chlorides. The recipe used in this trial did not contain any alkali chlorides and so this may explain why both the colour and glaze was patchy on all three of the test pieces.

Summary of trial 1:
From this trial it can be concluded that all three test pieces have been partially glazed and coloured by the IGM and that the lack of alkali chlorides in this formulation has meant that the CGM did not take place.

Trial 2:
This theory was tested in the next trial and 4% sodium chloride was added on top of glaze powder recipe 1a to produce glaze powder recipe 1b.

Figure 5: Fired test pieces cementation glazed with GP1b

Observations:

All three of the test pieces have been coated in a shiny turquoise glaze. The fired glazing powder was adequately porous and friable enabling objects to be removed from the glaze mixture with moderate force. The body strength enabled removal of objects from the glaze mixture. A breakage was incurred in one of the test pieces (fused silica body) when an attempt was made to remove adhered powder from the underside of the object using an abrasive ceramic block.
This trial demonstrates the role of alkali chlorides in the cementation process and shows a drastic improvement in glaze formation, glaze smoothness and the strength of colour imparted. This trial proves the opinion formed in the previous trial, that the test pieces from trial one were glazed by the IGM only. In this trial, it can be concluded that test pieces have been glazed by a combination of the IGM and CGM. The importance of the CGM for the success of cementation glazing has been demonstrated in this trial. The addition of 4% sodium chloride to the glaze powder has resulted in the successful glazing of all three test pieces with only slight variation in terms of colour and glaze thickness

Trial 3:

The aim of this trial was to produce a more even glaze colour and thickness and to reduce the extent of adhesion between the glaze powders and test piece through the use of calcium hydroxide instead of calcium carbonate and to improve the strength of the test piece by adding a flux to the body.

Glaze powder recipe GP1c
Sodium carbonate 35.3 %
Calcium hydroxide 35.3 %
Flint 23.5 %
Copper carbonate 5.9 %

The glazing powder was again prepared by mixing the dry ingredients in a ball mill for 8 hours to ensure a homogeneous mixture
In order to improve the strength of the test piece 2% talc was added on top of fused silica to act as a flux.

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Figure 6: Fused silica test piece fired in glaze powder GP1c

Observations:

Object was coated in a smooth and shiny turquoise glaze.
Glaze mixture was very porous and friable, resulting in easy removal of this object from the glaze powder with minimal effort
The body strength has been improved by the flux addition.
The distribution of both the colour and the glaze appears more uniform in this trial. There was a significant increase in the friability and porosity of the fired glaze mixture, resulting is the easiest removal of the fused silica test piece out of all the trials. This was due to the use of calcium hydroxide instead of calcium carbonate

Summary:

This is the final 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. The trials on the cementation glazing process have proceeded well and 3D printable bodies and forms are being developed for this particular process. During this 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.