

Investigation of Ceramic Firing Processes for Investment Casting Shell Molds

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Bachelor of Science

by

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Abstract

PCC Structurals aims to improve the quality and consistency of their ceramic mold production for their investment casting processes to decrease product loss figures. Although their current production processes result in acceptable quantities of high-quality molds, a significant percentage of defective molds are produced. These defective molds cause appreciable product loss due to casting defects and mold failure. Available literature dictates that high-quality investment casting molds must exhibit fracture strengths within a desired range in order to perform adequately. However, information regarding specific firing procedures which consistently result in ceramic mold strengths within this range is not readily available. To address this problem, a proposed project aimed to compare the resultant strength values exhibited by ceramic mold samples of various firing histories to quantify the effect of temperature on the firing process. Testing methods and analysis techniques to accomplish the project goals included mechanical bend testing to find the modulus of rupture (MOR) followed by statistical analysis of the experimental values to determine the significance of the results. Due to the outbreak of COVID-19, the scope of this project was altered to interpret the data obtained earlier in the school year and provide recommendations for future project iterations.

Key Words: Materials Engineering, Ceramic, Ceramic Shells, Investment Casting, Three-point Bend Testing, Modulus of Rupture

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Introduction

Stakeholders

The primary stakeholder for this project is PCC Structural. PCC Structural is a world class investment casting company, specializing in the precision casting of superalloys, aluminum, and titanium. Based in Portland, Oregon, they have various manufacturing facilities across the United States and Europe. They specialize in every step of the investment casting process, from solidification modeling to precision machining and protective coating services. This allows them the complete manufacturing ability of a wide range critical components for a variety of industries.

What is Investment Casting?

Investment casting is the production of engineering castings using an expendable pattern mold. The most common method of investment casting involves ceramic mold production. This production is characterized by the repetition of alternating layers of liquid ceramic slurry and dry refractory powder, “stucco”, to form an investment– or shell– around a wax pattern. After a sufficient number of layers is applied, the slurry is allowed to dry. Upon drying, the shell’s internal surface permanently matches the shape of the wax mold. The whole piece is then heated to melt and drain the wax without affecting the shell. Then, the empty shell is fired, resulting in a casting mold with high dimensional accuracy and limited waste material. The ceramic investment casting process involves ten generic steps (Figure 1). [1]

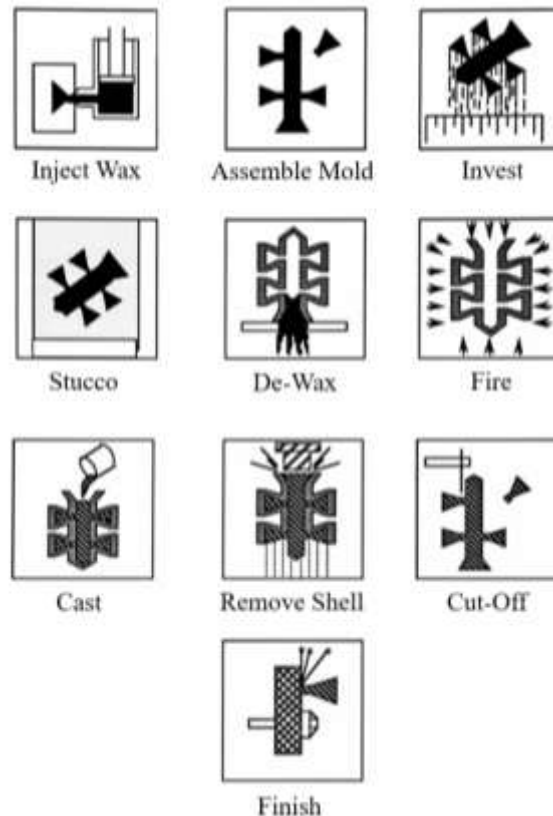


Figure 1. Graphical summary of typical investment casting process. Casting processes usually deviate from this generic example depending on the nature of the alloy being cast and the on the complexity of the component geometry. [2]

First, a metal die is produced with a component pattern. A wax mixture is injected into the metal die under pressure, molding the wax into the desired pattern. Once the pattern is solidified, it is removed from the die and assembled into a cluster with other wax patterns and mounted onto a wax runner system. This runner system is composed of passages and reservoirs which facilitate liquid metal flow and compensate for cooling contraction in the final casting mold. [2]

The finished wax patterns are then used to produce ceramic investments. The patterns are sequentially dipped into a ceramic slurry followed by a layer of dry stucco until the desired investment thickness is attained. Each coat is allowed to dry on the wax pattern before the next layer of slurry is applied. The grains of stucco that are deposited on the slurry coats after each dip serve the purpose to ease the mechanical stress associated with the drying process and ensure sufficient bonding between slurry coats. In most cases, the slurry and stucco applied in the first coating are different in composition than those used in subsequent coatings. Furthermore, the particle size of the stucco is increased with each dip. All slurries generally have three main constituents: a solvent (typically water), a liquid binder, and a refractory ceramic powder. Antifoam and latex can also be added to the slurry, depending on the solvent and the quality of dip needed. Stucco grains are all composed of refractory ceramics, sand-like in appearance. [2]

After the final slurry coat is added, the investment is allowed to dry. The result is a “green ceramic” which is solid, though not fully dense. The green ceramic also has its own corresponding “green strength”, which can be used for reference when comparing it to firing strengths. At this point in the process, the wax pattern is removed from the green ceramic via autoclave in a low heat process called dewaxing. In this process, heat from pressurized steam is transferred through the shell to the wax, which then melts and drains. [2]

The resultant cavity in the investment shell is an accurate replica of the original pattern. After the wax is removed, the ceramic mold is then fired at high temperature (typically from 800°C to 1100°C) to remove any residual wax and densify the ceramic shell such that it gains adequate strength for the casting process. Once the investment is fired, it is ready for casting. Specific casting procedures vary with the size and dimensional tolerance of the components and the material being cast. After casting, the shell is removed from the final component. The investment shell can be removed from the component through various methods, including but not limited to impact, vibration, grit-blasting, or chemical dissolution. [2]

Key Investment Casting Defects

PCC is mainly concerned with two types of casting defects—the most common types exhibited in their casting facilities: ceramic inclusions and hot tearing.

When molten metal is poured into a shell, it is highly reactive. Although ceramic materials are typically not considered to be reactive molten metal may still react with a ceramic shell. As a result, particles break off the inner surface of the shell and are embedded in the metal. These particles are known as ceramic inclusions. These inclusions can vary in size and morphology. Furthermore, the amount of penetration into the molten metal can vary widely.

This formation of ceramic inclusions has to do with the sintering of the ceramic mold. If a mold is sufficiently dense (and strong), the likelihood of particle separation and inclusion formation is reduced. However, research suggests that the absolute elimination of ceramic inclusions is not necessary. Ceramic inclusions which are below a critical size have a negligible effect on the mechanical properties of the cast component. Thus, it is highly feasible to decrease the

concentration of ceramic inclusions through the moderation of mold strength and densification. [3]

In contrast, when a ceramic mold is too strong, it can cause hot tearing. This phenomenon occurs during the final stages of solidification in molten metal. Immediately prior to this solidification stage, the bulk metallic material is a non-rigid semi-solid. Individual solid grains are formed however, a liquid metal phase exists along the grain boundaries. At this point, the solid grains are able to move freely. Thus, the bulk material is unaffected by stresses caused by the friction between solid particles and the investment wall. However, as solidification continues, the semi-solid metal becomes rigid as a dendritic network forms between grains across the liquid regions. At this point, the metal is rigid enough to transfer stress and strain though the bulk material but still considerably weak. Thus, cracks or hot tears can form as a result of the strain applied to the metal as it contracts while simultaneously catching or adhering to the investment wall. If the investment wall is not able to contract sufficiently with the metal component, hot tearing is inevitable. [4]

The likelihood of avoiding both of these defects increases when a ceramic mold performs within an ideal strength range. Establishing a quantitative means for finding this zone is main focus of this project.

Factors Affecting Ceramic Investment Strength

The strength of a ceramic component is largely determined by its flaws. Specifically, flaws act as stress concentrators which facilitate crack propagation and therefore decrease the effective strength of the bulk material. There is a large variety of flaws which affect resultant ceramic strength (Figure 2). To counteract flaw formation, densification and coalescence of the bulk material must be achieved. [5]

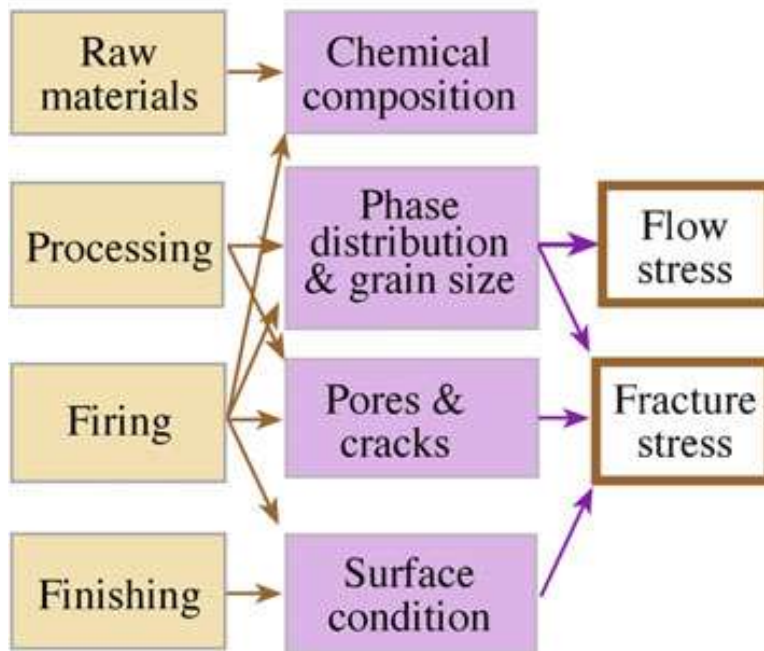


Figure 2. Factors affecting the mechanical properties of ceramics. Key factors including phase distribution, grain size, and porosity are directly dependent on the densification characteristics of the drying and firing processes. [6]

The traditional ceramics typically used in investment casting lack homogeneity and purity. It is difficult to induce bulk coalescence in investment ceramics as multiple phase transformations occur in different compounds simultaneously during the sintering process and the distribution of particle sizes amongst various ceramic phases is large. Thus, it is difficult to produce traditional ceramics with ideal strength properties. Firing at elevated temperatures and variance in ceramic constituent concentrations can be employed to increase the densification and coalescence of multiple heterogeneous phases—though doing so does not guarantee bulk densification. Alternatively, efforts can be focused on the densification of a single phase within the ceramic such that it acts as a network which strengthens the bulk material. In either case, facilitating the adequate densification of traditional ceramics, such as those used in investment casting, is key to obtaining ideal strength characteristics. [2] [5]

Densification of the Ceramic Investment

In investment casting, all densification processes are conducted at atmospheric pressure. Investments are processed with two general phases of densification: drying of the liquid slurry and firing of the green ceramic. The drying chemistry of the ceramic slurry is a two-part process in which gelation occurs simultaneously with the dewatering of the ceramic slurry. The firing process is a high temperature sintering process in which the final crystal structure of the ceramic material is established, refined, and permanently fixed. [7] [8]

Drying Chemistry

Most slurry binders are silica “sols” which are colloidal mixtures of solid silica particles evenly dispersed in a liquid. Sols are generally designed such that the small, dispersed particles (1 to 1000nm in diameter) remain dispersed in a liquid medium due to the repulsive intermolecular forces between individual, charged particles. This is critical for a sol to remain homogenous and to avoid the premature coagulation and sedimentation of large solid particles. [2] [8]

The stability of a typical investment slurry binder is tailored such that bulk gelation or solidification will occur due to a combination of its thixotropic properties and the simultaneous evaporation of its solvent liquid (water). Thixotropy is the ability of a sol to remain in a liquid state due to constant shear stress and then gain viscosity—to the point of gelation—upon resting. Thus, liquid ceramic slurries maintain excellent formability until they are applied to wax molds, at which point they solidify to match the shape of the wax. This shape is then retained as the solvent evaporates such that the thixotropic properties of the bulk material are non-reversible. [8] [9] [10]

In a simplified example of this sol-gel phenomena, aqueous silica particles are bonded to free hydroxide ions, rather than other silica tetrahedra. Once the silica particles are sufficiently concentrated due to the absence of shear and the evaporation of their solvent, they collide and polymerize, forming a three-dimensional network. Regardless of the degree of polymerization, the chains of silica which are formed entrap, bond with, and therefore solidify the dispersed refractory ceramics and stucco particles which are included in the bulk investment material. This results in a “green” ceramic (Figure 3). [2] [10]

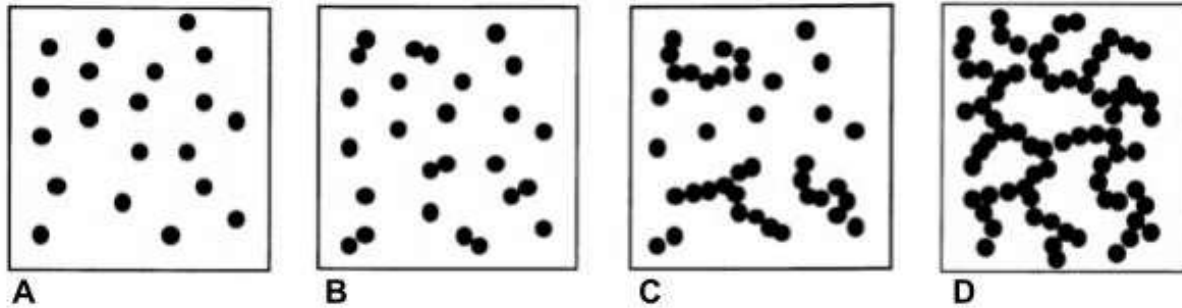


Figure 3. Two-dimensional, graphical representation of the gelation process of a typical silica binder. Each black dot represents an individual silica particle. The formations depict a colloid mixture (A), short chains of polymerized silica (B), bridging silica chains and microgel regions (C), and a continuous silica gel network (D). Refractory particles are entrapped in the large gaps between the chains of the three-dimensional silica network—producing a solid, green ceramic. [2]

The degree to which polymerization occurs is dependent on many rheological parameters in the drying process—not all of which are entirely understood. Specifically, increased temperature, decreased drying rate, and varied particle size have documented effects on the degree of polymerization and, therefore, the resultant microstructure of the dried ceramic material. For example, though it is generally assumed that the green investment ceramics have an amorphous structure, there are instances in which limited crystallinity can be attained during the drying process. [7] [10] [11]

The drying processes applied to investments are directly tied to the firing chemistry of the bulk material. If increased amounts of crystallinity and densification are achieved upon drying, the amount of densification during firing will improve. However, the degree of water loss, which varies based on the drying process, can have adverse effects on investment survival during firing. Specifically, green components with high water content are at high risk of steam explosion fracture during the firing process. Conversely, excessive drying can lead to bulk shrinkage which causes dimensional instability and cracking in the investment. [8] [10] [12]

Firing Chemistry

It is difficult to accurately predict the sintering behavior of the ceramic slurries used in investment casting as the firing chemistry of the green investments is dissimilar to that of other typical engineering ceramics. This is largely due to the inhomogeneous microstructure of ceramic slurries—specifically those which are applied and dried at atmospheric pressure. The kinetics of investment firing chemistry are driven by the variation of particle species, particle size distribution, and the resultant packing factor and porosity from the drying process. All of these factors, which are dependent on the microstructure of the green ceramic, determine which particles are grouped together, and which phases will form and react throughout the bulk material during the firing process. Thus, the randomness associated with inhomogeneity complicates firing procedures for ceramic investments. [5] [7]

Selecting proper pre-firing and firing cycles is of the utmost importance in managing the coalescence and sintering of multiple, inhomogeneous phases in an investment. A simplified example of the difficulty with which ceramic phases are controlled can be observed in the phase transformation paths of silica polymorphs—which are often present in investment slurries and binding agents. Silica polymorphs can be altered via two transformation routes: displacive and

reconstructive transformation (Figure 4). Each polymorph can be modified through displacive transformation in which stacking faults between silica sheets are accrued such that the crystal structure is slightly distorted. Thus, each polymorph can have varying, though analogous, crystal structures. [2] [8] [9]

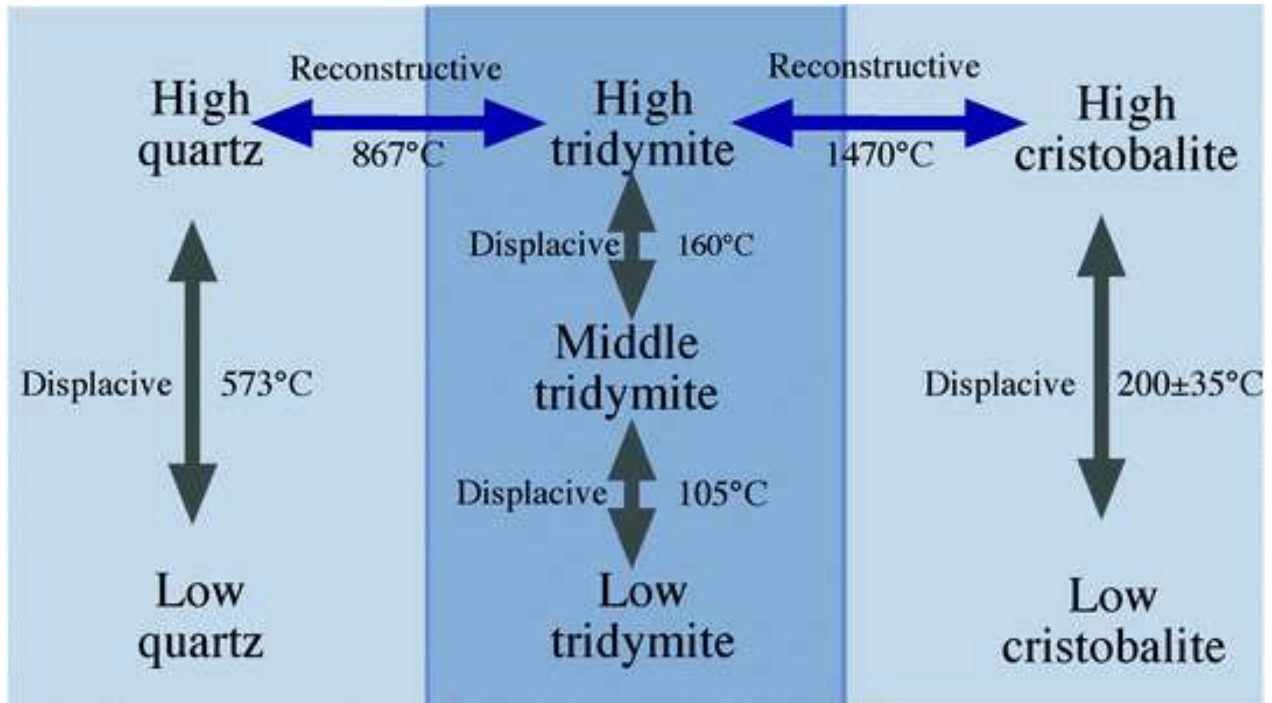


Figure 4. Graphical representation of silica polymorph transformation routes. The reconstructive transformation temperatures are significantly higher than those of displacive transformations due to the high level of energy required to modify bonds throughout the bulk material. Furthermore, the magnitude of difference in crystal structures defines which transformation paths are possible. For example, quartz cannot be directly transformed into cristobalite. [2]

Transformations from one polymorph to another (such as from quartz to tridymite) occur through reconstructive transformation in which Si-O-Si bonds, which connect silica tetrahedra, are broken so that new silica tetrahedron structures can form. Reconstructive transformations require a significantly higher amount of energy than displacive transformations because of the dissociation of covalent bonds. [2] [8] [9]

Further complications arise while promoting coalescence in investment ceramics given the relatively low purity of the refractory ceramic compositions of most slurries. Fortunately, only a handful of refractory ceramics are commonly used in investments. Even so, dispersed binary and ternary phases are common—each with their own set of polymorphs—and some are reactive with the surrounding material. The reactivity of dispersed phases can limit the ability of certain phases to coalesce and densify. [2]

Table I lists the most common refractory ceramics used in investment casting. In compositions with listed volume percentages, the remaining volume is occupied either by the secondary species listed or by various, naturally occurring mineral compounds. Notice how in the calcinated china clay, sillimanite, mullite, and fireclay grog compositions, there are large remainder percentages of non-listed material. This is due to the fact that these minerals are

naturally occurring and are therefore predisposed to have inhomogeneous compositions which include a variety of other, often complex, minerals. [5] [7] [8]

Table I Common Investment Refractory Ceramics and Their Compositions [2]

Refractory	Composition	
Silica	SiO ₂	
Alumina	Al ₂ O ₃	
Chromic Oxide	Cr ₂ O ₃	
Magnesia	MgO	
Zircon	ZrSiO ₄	
Zirconia	ZrO ₂	
Calcinated China Clay	Al ₂ O ₃	42-44% Alumina by Volume
Sillimanite	Al ₂ O ₃ and 2SiO ₂	60-65% Alumina by Volume
Mullite	3Al ₂ O ₃ and 2SiO ₂	56-79% Alumina by Volume
Fireclay Grog	Al ₂ O ₃ and 2SiO ₂	40-80% Alumina by Volume 10-40% Silica by Volume

Thus, further considerations must be made as more energy is required to promote sufficient transformation and coalescence between multiple incongruent phases. Energy can be added to the system via increased firing temperature. Alternatively, adjusting the concentration of reaction and binding agents in the slurry promotes the formation of specific compounds and microstructures during firing. Although firing times can be increased to improve sintering as well, excessive increases in production time are unfavorable for industry applications. [2] [5] [7] [8]

Preliminary Bend Tests

PCC Structurals required the completion of preliminary bend tests for two reasons. Firstly, the control data from the preliminary tests would offer insights regarding the capabilities of our testing equipment and the effectiveness of our firing and testing methods. Secondly, the control data acquired would offer useful comparisons to future bend tests to quantify the effect of firing temperature on shell strength.

Two sets of samples were produced. The first set was tested by PCC Structurals in Portland, Oregon. The second set was tested at Cal Poly. In these three-point bend tests, the strengths of shell samples were quantified by experimentally obtained Modulus of Rupture (MOR) values. The testing procedures conducted at Cal Poly followed common practices utilized by PCC Structurals and the guidelines of ASTM standard D790. [13]

Procedure

Upon receiving the Cal Poly samples, inconsistent cross-sections were observed. Many of the samples had excess slurry along the edges which altered their otherwise rectangular cross-sections (Figure 5). To ensure the accuracy of the bend test, a regular, rectangular cross-section is optimal. Thus, the edges of the Cal Poly samples were ground flat using a Dremel prior to firing. [13]

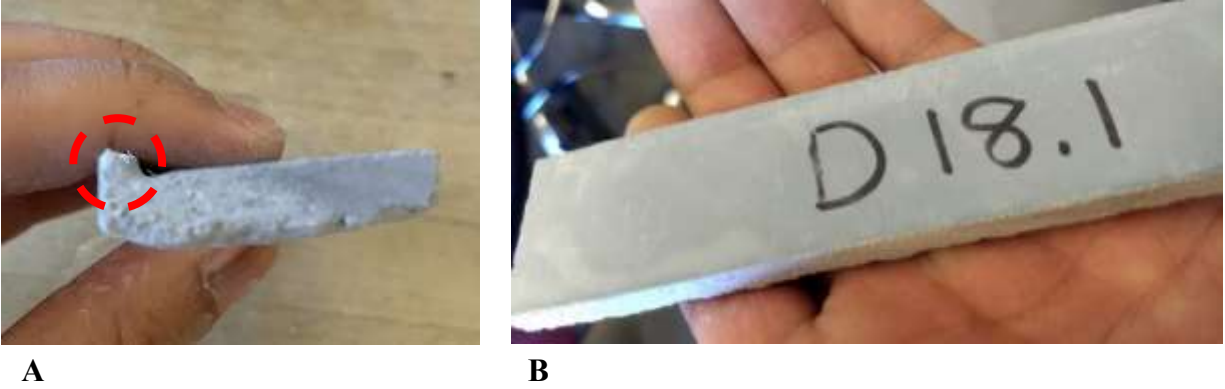


Figure 5. A typical cross-section of a bend test sample received from PCC Structural (A) and a finished, Dremel-ground sample (B). Note that processing the samples with the Dremel adds the risk of flaw formation due to handling.

Both the Portland and the Cal Poly sample sets were separated into three groups, based on varied stages of completion of a standard firing procedure provided by PCC Structural (Figure 6). The first group was referred to as “green samples.” They experienced no firing procedure. The second group was referred to as “elevated temperature samples.” This sample group experienced an incomplete firing cycle. The elevated temperature samples were loaded into a ramping furnace which was preheated to and held at 1200°F (649°C). After thirty minutes, the ramp furnace was programmed to increase the temperature to 1625°F (885°C) at a rate of 212.5°F/hr. (100°C/hr.). The elevated temperature samples were held as this temperature for one hour and were then left to air cool overnight. The final group was referred to as “fired samples” as they experienced the complete firing cycle. In addition to the previous ramp furnace procedures, the fired samples were loaded into the ramp furnace which was preheated to 1800°F (982°C). The fired samples were soaked at this temperature for three hours and air cooled overnight.

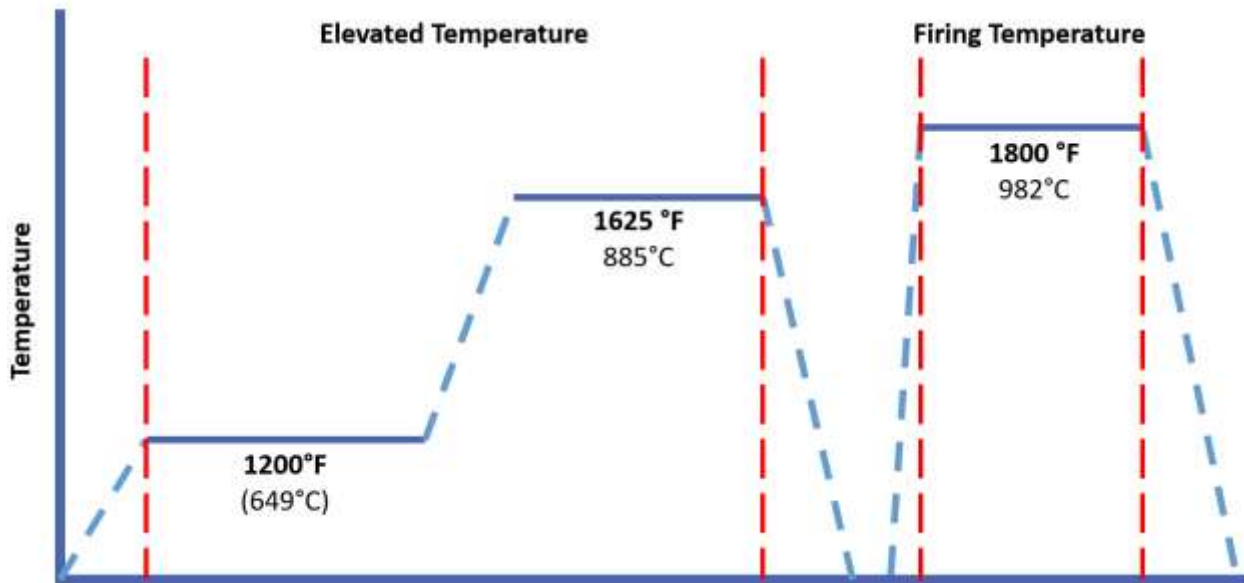


Figure 6. A schematic representation of the firing cycle recommended by PCC Structural. Although there are three distinct temperature regions, this firing cycle is considered to have two parts: the elevated temperature region and the firing temperature region. In the context of the previous project plans, varying the temperature of the firing temperature region was the focus of the study.

After the samples were fired, they were subjected to three-point bend tests which followed ASTM standard D790-17. The samples were tested in batches according to their respective firing cycle groups. Before each test, the sample dimensions were measured using digital calipers and recorded for MOR calculation. The testing apparatus used was an Instron Universal Testing Machine with three-point bend test fixtures. A support span length of four inches was set in the three-point bend test fixture. Custom testing parameters were programmed using Bluehill software according to ASTM D790-17.

Initially, a percent deflection of 40% was used. However, this testing parameter yielded inconclusive results—the automated test would stop before a discernable yield point was observed in the load-displacement curve and before the samples exhibited visible fracture and failure characteristics. Thus, the percent deflection was changed to 70% so that the test would consistently result in definitive yield points and visible failure, respectively. Maximum load was used, but samples consistently failed before 25 lbf was applied. MOR values were calculated according to ASTM D790-17.

Safety

It is important to keep in mind that three-point bend testing is a mechanical test taking place in a laboratory setting. Proper personal protective equipment should be worn while conducting these tests. This includes long pants and closed-toed shoes, with long hair tied back and safety glasses on. Baggy clothing is less of a risk in this setting compared to others, but it still may get caught on some part of the machine and could injure someone or damage the machine, so it is advised to not wear it. One should be cautious of their surrounding and be watchful for any tripping or fire hazards. [14]

The machine being used in this study is the Instron Universal Testing Machine with three-point bend testing fixtures. These fixtures are installed using pins and holes, so one should ensure that these holes are properly aligned, and the pins are completely inserted before loading any samples or starting a test. The fixtures should be loaded while the machine is off or unable to start a test, to prevent injury. To avoid machine malfunction and the potential damaging of equipment, before turning on the machine one should ensure that the knob on the left-hand side of the loading zone is secure to stop any test from going astray. Always use the polycarbonate shield while running a three-point bend test. [14]

Results and Discussion

Box plots of the MOR values for both the Cal Poly and PCC Structurals sample sets were produced (Figure 7). The Cal Poly bend test data resembled PCC's test data. However, the Cal Poly MOR values were consistently lower. The variance between the two sample sets could be considered negligible, given the scatter associated with ceramic test samples and the small sample size of MOR bars considered. However, it is possible that the higher MOR values are a result of the cross-sectional inconsistency of the PCC samples since they were not ground down to have rectangular cross-sections like the Cal Poly samples were. According to common practice, a rectangular cross-section yields the most accurate test results and is essential for successful bend tests. Conversely, it is possible that the grinding and handling of the Cal Poly samples caused the formation of microcracks, resulting in lower MOR values. [13]

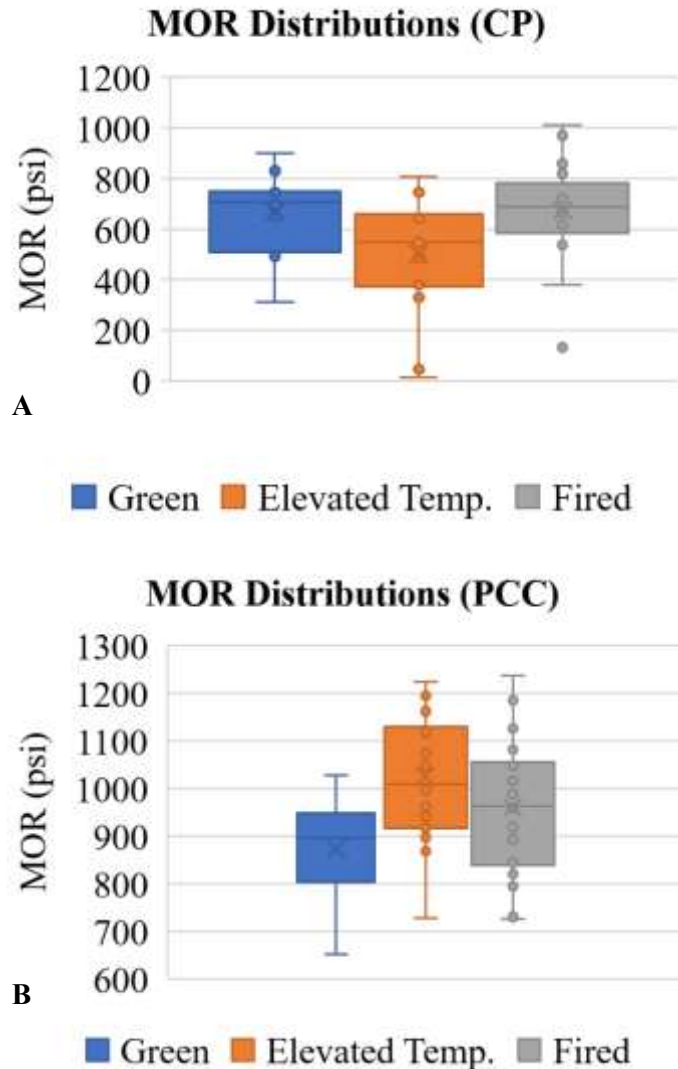


Figure 7. The modulus of rupture (MOR) distribution obtained the Cal Poly three-point bend test samples (left) and the PCC Structurals three-point bend test samples (right). Though the scales of the two plots are different, the order of trends in MOR values as a response to firing are relatively consistent. This indicates that similar phenomena may have occurred in both sample sets.

Despite the differences observed between the two sample sets, the most important data trend observed is the lack of change between the MOR values according to firing cycle completion. Specifically, in both sample sets, there is negligible change between the average MOR values of the green samples and the fully fired samples. This fact is contrary to the common understanding of ceramic firing theory. Without a doubt, a certain amount of coalescence and densification occurred during the firing process in multiple phases present in the samples. Why, then, would the bulk material of each sample not exhibit definitively increased strength?

Through extensive materials characterization and microstructural analysis, it has been conjectured that the networks of gelled silica present in a typical, investment are the principal load-bearing components of concern in the ceramic microstructure (Figure 8). Furthermore, it is assumed that—despite any coalescence which may occur within specific phases throughout the

ceramic material—the coalescence and crystallization of the silica binder network is the key to increasing strength in the bulk material. [2]

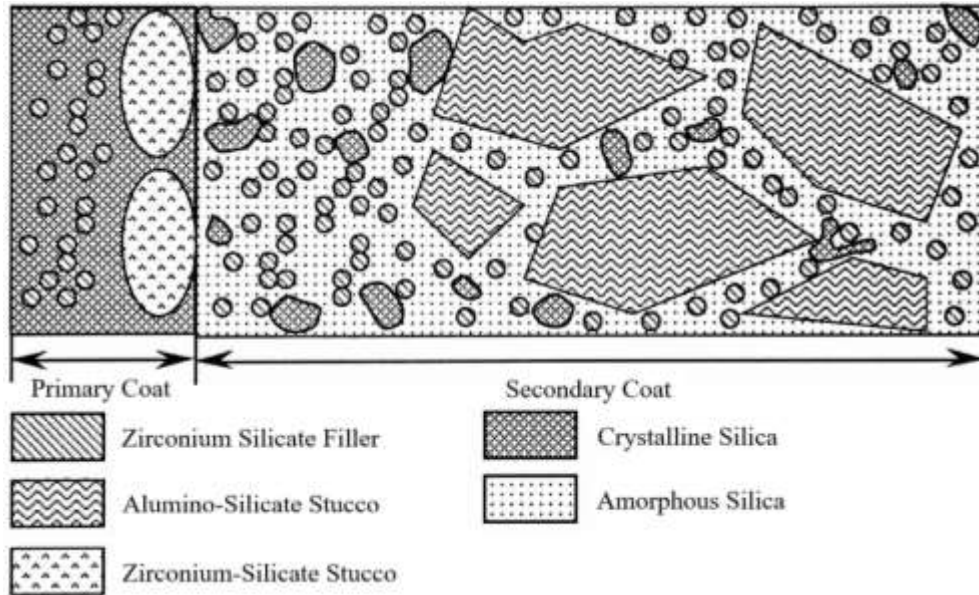


Figure 8. Graphical representation of a typical investment shell microstructure. This depiction of the silica gel network shows how the gel is a key load-bearing component in the investment shell as the dispersed phases are not continuous. The stark contrast between the crystallization behavior of the primary coat and secondary coat is to be expected given that the nature of the binders and additives used exclusively for primary coats. [2]

According to multiple studies, the crystallization of the silica gel does not typically occur at temperatures below 1000°C. In fact, crystallization is thought to *start* at 1000°C. Therefore, as the firing temperature used was approximately 982°C, it is unlikely that sufficient crystallization of the silica binder network occurred. Furthermore, as the binder is the key load-bearing constituent, it is possible that the lack of silica crystallization resulted in the negligible change in strength observed between the green and fired samples. [2] [15]

Future Project Recommendations

Revised Examination of Firing Temperature vs. Flexural Strength

As stated in the analysis of the preliminary bend test results, it is possible that the samples in question were not fired at sufficiently high temperatures to facilitate both the densification and devitrification of the silica binder phase within the bulk investment material. Thus, the goals of this project may be realized in the future with the use of an alternate firing cycle with an increased firing temperature (Figure 9). [2]

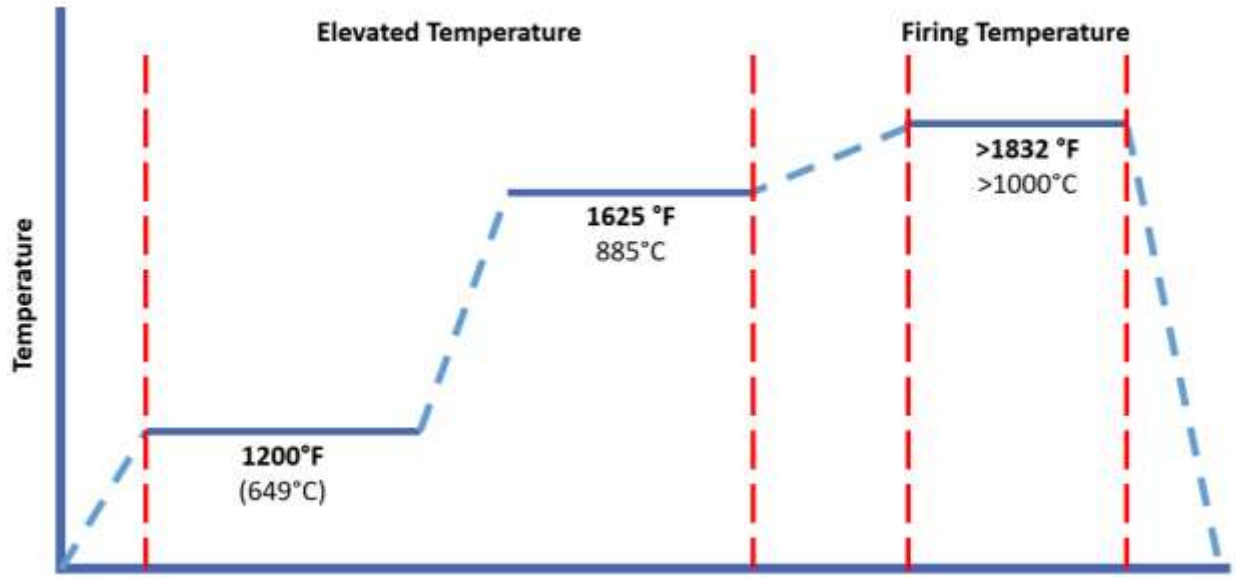


Figure 9. An alternate firing schedule which would potentially result in more sensible MOR values. Studies which show the definitive devitrification of silica binders typically utilized firing temperatures of 1000°C or more. Furthermore, the cooling region in the middle of the previous firing cycle can be eliminated to increase efficiency. [2]

One major issue with this recommendation is the furnace capabilities available at Cal Poly. This was a limiting factor in the previous project plans as the furnaces are only able to reliably hold temperatures less than or equal to 1000°C. Thus, the following recommendation may prove to be more favorable to Cal Poly Students.

Drying Temperature vs. Reconstructive Crystallization Temperature

In light of Cal Poly's furnace temperature limitations, methods for inducing the devitrification of silica binders at lower temperatures should be explored. The effect of ceramic and metallic impurities on the kinetics concerning silica crystallization are well documented. It has been found that the amount of impurities must be optimized such that the mobility of silica particles is increased by reactive impurities but not impeded by the overcrowding of dispersed phases. Specifically, in one study it was found that a gel with 2% alumina featured increased cristobalite formation. However, any more or less resulted in inferior crystallization behavior. [2] [15]

The design of custom binder systems may be outside the scope of senior projects at this time. However, structural water content in the gelled silica network could be evaluated as a devitrification agent. It has been conjectured that residual hydroxide ions (structural water) could act as an oxidizing agent which balances the stoichiometric concentrations of oxygen and silicon in the glassy, amorphous silica phase thereby increasing the likelihood of crystallization. Similar to the concentration of ceramic and metallic impurities, there is presumably an optimal concentration of structural water which can be attained through a specific drying process. [2] [15]

A future project could be designed to quantify the correlation between structural water reduction (drying) and crystallization behavior. Many factors affect the drying process but the most feasible to control is the drying temperature. Additionally, if structural water reduction does have an effect on the kinetics of crystallization, then it may be possible to produce samples with

significant amounts of crystallization with firing temperatures below 1000°C (within Cal Poly's furnace temperature limitations). Thus, a reasonable project could vary the drying temperature of test samples and then examine if the effect of drying level is significant enough to lower the crystallization temperature of a silica gel.

The preliminary bend test samples were dried by PCC Structurals at a temperature of 300°F (149°C) for 3 hours as a common practice to ensure sufficient drying. Since the preliminary test samples failed to show signs of crystallization, the proposed project could examine drying temperatures above and below this drying temperature. If a statistically significant correlation is found, then the test methods could potentially be applied to investments with alternate binder systems.

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