An introduction to ceramic forming processes

Antonio Licciulli
The slip casting process

- Slip casting is the process of filling a porous mould (1), usually a gypsum mold, with a ceramic slurry (3).

- The water is removed from the slurry via capillary action through the small pores in the mold (4). As the water is removed the ceramic particles are collected against the surface of the mold.

- This process is allowed to continue until the correct thickness (2) is achieved, after which the remainder of the slip is drained out of the mold.

- The green body is dried further and removed from the mold. After the green body is removed it is dried and fired so that it can go through the final machining process.

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The slip casting process
Slip casting at a glance
Benefits and drawbacks with respect to dry forming processes

**Advantages**
- Low capital investment required to start the production
- Highly homogeneous slurries and ceramics can be produced
- A wide variety of complex and big shapes can be produced that could not be produced using other conventional methods.

**Disadvantages**
- Lower dimensional precision can be achieved compared to dry pressing or powder injection molding.
- The production rate is lower than the rate of dry pressing, injection molding or extrusion.
- Differential shrinkage can be caused by a packing factor gradient that can be induced in the molds during water removal.
- The molds that are used have a low toughness so they can fracture easily therefore a large mold inventory must be maintained to insure a constant production rate.

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Slip Casting as forming method of ceramic CAD/CAM blocks

<table>
<thead>
<tr>
<th>Forming Methods</th>
<th>Raw material</th>
<th>homogeneity</th>
<th>Tolerance</th>
<th>Productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Isostatic Pressing</td>
<td>Powder</td>
<td>1-2%</td>
<td>± 0,5% (± 3%)</td>
<td>high</td>
</tr>
<tr>
<td>Die Pressing</td>
<td>Powder</td>
<td>3-10%</td>
<td>± 0,5% (± 1-3%)</td>
<td>Very high</td>
</tr>
<tr>
<td>Extrusion</td>
<td>mixture</td>
<td>Bad because of high binder content</td>
<td>± 1,5% (± 3-5%)</td>
<td>Low because of debinding and dry time</td>
</tr>
<tr>
<td>Solid Casting</td>
<td>slurry</td>
<td>good</td>
<td>± 0,5% (± 3-5%)</td>
<td>Low because of dry time</td>
</tr>
<tr>
<td>Injection Moulding</td>
<td>mixture</td>
<td>Bad because of high binder content</td>
<td>± 1,5% (± 3%)</td>
<td>Low because of debinding and dry time</td>
</tr>
</tbody>
</table>

Advantages

- Economy of process
- Very low shrinkage (14-15% vs. 20-25% of other forming method)
- High homogeneity
- No or very less organic binders

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Solid casting: concentrated slurry homogenization, pour into mold, dehydration, demolding drying, presintering, sintering;
Silica cores made with solid casting

- Silica cores are formed by slip casting in precision plaster molds. The design resembles the investment casting process.

- Sprue and risers, the passages through which the slip is introduced into a mold. The term also refers to the excess material which solidifies in the sprue passage.
Solid cast blocks are blocks obtained by solid casting are polished, cut, turned on a lathe with very tight tolerances.

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Machinable ZrO$_2$

- The new slip casting forming process of zirconia blocks allows: very high strength, lower shrinkage compared to dry pressed materials

- The project has been funded by Regione Puglia and jointly developed by Salento University and Salentec, on January 2010. Salentec received the ISO 9001 and ISO 13485 certification.
Forming of new zirconia for biomedical applications

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The preparation of the slip

The mixtures of powders binders and additives for the preparation of suspensions and granules are mixed and homogenized in horizontal rotary mills with ceramic beads to act as a grinding media.
Thermal deformations
Thermal and pyroplastic deformations

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Pyroplastic anisotropic behavior and sintering shrinkage

\[ \varepsilon = \varepsilon_e + \varepsilon_v + \varepsilon_t \]

\[ \varepsilon_e = \frac{\sigma}{E} \quad \text{Elastic Strain} \]

\[ \varepsilon_v = \frac{\sigma}{\eta} t \quad \text{Viscous strain} \]

\[ \varepsilon_t = \alpha \Delta T \quad \text{Thermal strain} \]
Traditional mould design method

- Difficult to predict the deformations of complex shape during production process
- Mould design is performed by means of a long iterative and labour intensive process;
- High time and costs to produce new series;
- Ceramic companies have a limited flexibility and capacity to react to market changes

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CNC manufacturing of washbasin model

By means of this CAD model, a CNC machine can produce the polyurethane model in green or fired size, allowing the customer to check and approve the model before next activities.
Case mould

- On the basis of CAD model, it follows design of the mould and case-mould.
- In the mould design all technical aspects needed for the construction are decided and set: position of internal feeding pipes, back circuit lay-out, centering devices, plates and frames.
- Case-mould CAD design allows the CNC machine to produce the tool by machining a resin or plaster block.
- The case-mould obtained in this way can be now used for casting the resin working mould.

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Mould fabrication

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Plaster of paris the master of modelers

- Gypsum plaster, or plaster of Paris, is produced by heating gypsum to about 300°F (150 °C)
  \[
  \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2} \text{H}_2\text{O}
  \]
- When the dry plaster powder is mixed with water, it re-forms into gypsum:
  \[
  \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
  \]
- The setting of unmodified plaster starts about 10 minutes after mixing and is complete in about 45 minutes
- If plaster or gypsum is heated above 392°F (200°C), anhydrite is formed, which will also re-form as gypsum if mixed with water
Slip casting and demoulding
Comparison between model and sintered
Plaster secrets revealed

- The pores present have a size between 0.2 and 30 microns.
- The majority of the pores have a size between 1 and 3 uM.
- This distribution provides the sucking as much as 56-57% of the initial content of water suspension.

Summary of Hg tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cumulative volume (cc/g) :</td>
<td>0.4818</td>
</tr>
<tr>
<td>Total specific surface area (m²/g) :</td>
<td>0.822</td>
</tr>
<tr>
<td>Average pore radius (Micron) :</td>
<td>1.738</td>
</tr>
<tr>
<td>Total porosity (%) :</td>
<td>55.72</td>
</tr>
<tr>
<td>Bulk density (g/cm³) :</td>
<td>1.16</td>
</tr>
<tr>
<td>Apparent density (g/cm³) :</td>
<td>2.61</td>
</tr>
</tbody>
</table>

SEM morphology of plaster microstructure
Gypsum mold: strength vs porosity

- The molds used for slip casting usually have a low toughness.
- Their porosity lowers the strength.
- To increase the strength some porosity must be sacrificed.
- Low strength gypsum molds wear out with time.
- These molds are great for producing complex shapes because as the green body loses water and begins to dry out it shrinks away from the edges of the mold for easy removal.
High pressure casting in resin molds

High-Pressure (8-30bar) slip casting in resin moulds is the more advanced technology.

Considering the high cost and short lifespan of traditional casting moulds, and the cost of disposing of the exhausted moulds, the creation of microporous resin moulds is the latest discovery in the production of ceramics.

The stages leading to construction using this technology are the same as in a normal, traditional production cycle. The model and first mould are constructed and a matrix die is created in epoxydic or environmentally-friendly resin.
Micro-porous resin moulds advantages over plastic

- Micro-porous resin moulds can run at least 20,000 cycles
- Small pore diameter - reduced pore clogging
- High strength - high duplicate moulding rate
- Less deformation in the working mould of the pressure casting system
- Minimal shrinking
- Reduced plastic mould production therefore also lower mould costs
- Reduced production downtimes thanks to reduced mould change requirements
Capillary suction on the slip

$$\Delta P = 2\gamma \cos \theta / R_c$$

- $\Delta P$ = suction,
- $\gamma$ = surface tension
- $\theta$ = angle
- $R_c$ = radius of curvature

The flow of liquid through a porous medium is:

$$\frac{dV}{dt} = \frac{K}{n} \times \frac{dP}{dx}$$

- $dP/dx$ = the pressure gradient across the filter
- $n$ = filtrate viscosity,
- $dV/dt$ = volumetric flow rate of the filtrate and $K$ is the filter permeability
Cast thickness as a function of casting time

\[ L = \left[ \frac{2J\Delta Pt}{nR_c} + \left( \frac{R_m}{R_c} \right)^2 \right]^{1/2} - \left( \frac{R_m}{R_c} \right), \]

- \( L \) = cast thickness
- \( J \) = vol. of cast/vol. of liq. Removed
- \( R_c \) = resistivity to liq. transport in the cast,
- \( \Delta P \) = apparent mold suction
- \( n \) = viscosity of liq. transported
- \( R_m \) = liquid transport resistance of the mold

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# Defects in Cast

## TABLE 25.6 Defects in Casts

<table>
<thead>
<tr>
<th>Macroscopic Defects</th>
<th>Microscopic Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable wall thickness</td>
<td>Large pores</td>
</tr>
<tr>
<td>Differential wall thickness</td>
<td>Particle size segregation</td>
</tr>
<tr>
<td>Shape distortion</td>
<td>Particle density segregation</td>
</tr>
<tr>
<td>Macroscopic cracks</td>
<td>Small cracks, laminations</td>
</tr>
<tr>
<td>Voids within the part</td>
<td>Packing fraction gradients</td>
</tr>
<tr>
<td>Voids on mold/cast surface</td>
<td></td>
</tr>
<tr>
<td>Bubbles in cast</td>
<td></td>
</tr>
<tr>
<td>Pin holes</td>
<td></td>
</tr>
<tr>
<td>Wavelike drained surface</td>
<td></td>
</tr>
<tr>
<td>Uneven drained surface</td>
<td></td>
</tr>
</tbody>
</table>
Viscosity of Slurry

- viscosity too high or low: not ideal
- slurry may have yield strength
- good stability for storage life

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Gel Casting

- Refer to cases where binder (monomer) can polymerize, make system a gel; fill in a mold (of complex shape) → stimulate reaction to gelation → de-mold → thermal treatment to product

- Can be used for dense product or porous product, former case: concentrated slurry to get high density packing

- Mold not necessary porous material, can be made of a variety of materials
Gel casting

- Refer to cases where binder (monomer) can polymerize, make system a gel; fill in a mold (of complex shape) stimulate reaction to gelation de-mold thermal treatment to product

- Mold can be made of a variety of materials

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Centrifugal Casting

- Sedimentation: slower rate; add centrifuge to increase rate of sedimentation
- Well dispersed suspension, very slow sedimentation, can reach higher density; different particle size, different rate $\rightarrow$ different effect, i.e. may be size distribution inside the cake (sediment) $\rightarrow$ to product, poor effect $\rightarrow$ always differential shrinkage
- Centrifugal casting: suitable for tube making; $r\omega^2$ for $g$ as the acting force

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Dip moulding

Dip moulding is essentially a technique for the economical production of flexible and semi-rigid plastic components. Often used for mass production, it is particularly suitable for medium and small quantities.
All ceramic crowns from dip moulding

A dental prosthesis manufacturing method based on CMC has been patented

chopped fibers reinforced CMC microstructure

The tooth replica is immersed in to a special ceramic slurry

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Tape Casting

- Also called doctor blade method; often used to fabricate thin, plate-like products, such as substrate.

- High productivity, if continuous process, green tape first, then cut into appropriate sizes;

- Suitable for multilayer “laminated” products.

- Anisometric particles may align preferentially during casting, to form special structure;

- Tapes of Tyflon, Mylar are often used as carrier.

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Common tape casting equipment

Fig. 26.6 Schematic of continuous tape casting machine.

from JS Reed, 1995

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Doctor Blade

Belt moving velocity + pressure gradient $\rightarrow$ effect of motion

\[
\frac{dp}{dx} = -\left(\rho g L + P_{\text{applied}}\right)/W = \frac{d\tau_{xy}}{dy}
\]

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Uniformity Issue

High rate and high viscosity, beneficial to product uniformity

Industrial scale: 25 m long, several meters wide, 1500 mm/min speed, tape thickness: 25-1250 µm are common;

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Some problems and some solutions

<table>
<thead>
<tr>
<th>Problem</th>
<th>bubble</th>
<th>skinning</th>
<th>crack</th>
</tr>
</thead>
<tbody>
<tr>
<td>More solvent</td>
<td>decrease</td>
<td>NA</td>
<td>may increase</td>
</tr>
<tr>
<td>Higher temperature</td>
<td>decrease</td>
<td>increase</td>
<td>NA</td>
</tr>
<tr>
<td>Increase solvent evaporation rate</td>
<td>NA</td>
<td>increase</td>
<td>increase</td>
</tr>
<tr>
<td>Faster pouring rate</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Air rate up</td>
<td>NA</td>
<td>NA</td>
<td>increase</td>
</tr>
<tr>
<td>Inorganic</td>
<td>NA</td>
<td>lower</td>
<td>NA</td>
</tr>
</tbody>
</table>

Ideal slip: high solid content, low viscosity, solvent not causing skinning and trap air bubble, drying system can remove gas and rapid drying.
Electrophoretic casting

- Charged particles can be attracted and consolidated on a oppositly charged conductive substrate
- The electrophoretic deposition of particles onto conductiong substrates has been investigated for forming tubes and coating
- Cross section must be limited in thickness because the casting thickness is relatively slow
Dip Coating

- Pull at an angle and speed to get coating;
- Film thickness depend on slurry rheology; for Newtonian fluid

\[
\frac{\partial \tau_{xy}}{\partial y} = \rho g \sin \alpha
\]

\[
h_{\text{max}} = \sqrt{\frac{U \eta}{\rho g \sin \alpha}}
\]

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Dip Coating

Antireflection coating on 3,2x2,4m float glass

AR pilot plant in Campi Salentina (LE)

Mirror effect due to TiO₂ coating

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