PRESSURE SLIP CASTING METHOD FOR PRODUCTION OF CERAMIC COMPACT PARTS

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Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Mechanical Engineering
Boğaziçi University
2006

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my thesis supervisors Prof. Mahmut A. Savaş and Prof. Sabri Altıntaş for their invaluable suggestions support and guidance during the completion of this study. Prof. Turan Özturan, and Assist. Prof. Nuri Ersoy and Dr. Metin Yılmaz are also appreciated for their participation to the thesis committee. I am also grateful to Osman Civelek for his invaluable support in the experimental work.

Finally, I would like to thank my parents for their constant encouragement and endless support.

ABSTRACT

PRESSURE SLIP CASTING METHOD FOR PRODUCTION OF CERAMIC COMPACT PARTS

The fundamentals of slip casting method is based on the slip gets into form of the mold by the water absorption caused by the means of capillary forces formed on the porosities of the mold after powder suspension is poured plaster of paris mold. Pressure slip casting method is developed due to the life of plaster of paris mold is short and the duration of the process is long. In this method instead of plaster of paris mold, the molds made from polymers are used and the water in the suspension is taken out by the means of pressure. This method has more advantages because of the duration of the process is much shorter and the life of the pattern is much longer.

Among the high technology ceramics, Al_2O_3 (alumina) has the widest application due to its resistance to high temperatures and high wear resistance. In this study, aluminium oxide ceramic parts were produced by the slip casting and pressure slip casting methods. Ceramic powders ($Al_2O_3 \sim 1\ \mu m$) were mixed with distilled water and the dispersant (sodium silicate) ball milled in a ceramic jar for a long time in order to reduce particle size. Plaster of paris mold was used in the slip casting applications. The studies of two molds were carried out for the pressure slip casting method. The designed molds comprised basically two main parts. The alumina ceramic slip was formed by the means of pressure application with the mold that joined to the hydraulic pres. The parts in the same shape and dimension were produced by a plaster of paris mold for comparison. The sintering process was carried out after having enough samples. The parts, produced using the two methods, were examined in the micro structure characterization, shrinkage, porosity and three point bending tests. Weibull analyses were done and the results were evaluated.

ÖZET

SERAMİK PARÇALARIN ÜRETİMİ İÇİN BASINÇLI SLİP DÖKÜM YÖNTEMİ

Slip döküm yönteminin esası, toz süspansiyon malzemenin alçı kalıba boşaltıldıktan sonra, kalıptaki boşluklarda oluşan kapiler kuvvetler sayesinde suyun emilerek malzemenin kalıbın formunu alması esasına dayanır. Alçı kalıbın ömrünün kısa olması ve işlemin süresinin uzun olmasından dolayı basınçlı slip döküm yöntemi geliştirilmiştir. Bu yöntemde alçı yerine daha çok polimer malzemeden yapılan kalıplar kullanılmış ve basınç yardımıyla süspansiyon içerisindeki su uzaklaştırılmıştır. Bu yöntem, işlem süresinin çok daha kısa olması ve kalıp ömürlerinin çok uzun olması sebebiyle daha avantajlıdır.

İleri teknoloji seramiklerinin içinde, yüksek sıcaklık ve aşınma dayanıklılığına göre Al_2O_3 (alumina), en geniş uygulama alanına sahiptir. Bu çalışmada, slip döküm ve basınçlı slip döküm yöntemi ile alüminyum oksit seramik parçalar üretildi. Seramik tozları ($Al_2O_3 \sim 1\ \mu$ m), distile su ve dağıtıcı (sodyum silikat) belirli oranlarda karıştırılarak, seramik değirmenlerde tanecik boyutlarının daha da küçülmesi için uzun süre öğütülmeye tabi tutuldu. Slip döküm uygulamalarında alçı kalıp kullanıldı. Basınçlı slip döküm yöntemi uygulaması için iki kalıp çalışması yapıldı. Hazırlanan kalıplar temelde iki ana bölümden oluşmaktaydı. Bu kalıplar hidrolik prese bağlanarak, alumina seramik süspansiyon, basınç uygulaması yardımıyla, kalıpla şekillendirildi. Aynı şekil ve büyüklükte parçalar, karşılatırma amacıyla bir de alçı kalıpla üretildi. Yeterli numunenin elde edilmesinden sonra sinterleme işlemi yapıldı. İki yöntemle hazırlanmış olan parçalar, mikro yapı karakterizasyonu, küçülme, boşluk ve üç nokta eğme testlerine tabi tutuldu. Weibull analiz yapıldı ve sonuçlar değerlendirildi.

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LIST OF SYMBOLS/ABBREVIATIONS

a_m	Largest crack size
b	Width of the beam
c	Volume fraction of solids in the slip
d	Depth of the beam
D_f	Filter thickness
D_s	Thickness of the body
E	Elastic modulus
K_{IC}	Fracture toughness
m	Weibull modulus
M_r	Maximum moment in the beam
n	Mass balance factor
P	Total pressure effecting filtration
$P_s(V_0)$	Survival probability
s	Specific surface area of gypsum
S	Shrinkage value of specimen
S_1	Initial diameter of specimen
S_2	Final diameter of sintered specimen
t	Filtration time
ΔT	The maximum temperature drop
W	Water absorption
W_f	Filter resistance
W_s	Filtration resistance of body
W_1	Dry weight
W_2	Final weight after water absorption
η	Viscosity of the suspending medium
γ	Contact angle
ξ_c	Cast layer thickness
ξ_m	Position of the filtrate air interface in the mold

ξ_s	Position of the suspension-air interface during filtration
ξ_s^0	Position of the suspension-air interface at t =0
σ	Surface tension of water
σ_c	Compressive strength
σ_r	Modulus of rupture
σ_{TS}	Tensile strength

1. INTRODUCTION

Ceramics are hard, brittle solids. When designing with metals, failures by plastic collapse and by fatigue are the primary considerations. For ceramics, plastic collapse and fatigue are rare problems; it is brittle failure, caused by direct loading or by thermal stresses, that is the overriding consideration [1].

The history of ceramic processing technology is interesting in that both simple processes developed in ancient times for natural materials, and recently developed, relatively sophisticated processes dependent on synthetic materials are used extensively at the end of the 20th century [2].

Hand mixing, hand building and slip decorating of earthenware date back to before 5000 BC. The first forming machine was the potter's wheel, which was used earlier than 3500 BC for throwing a plastic earthenware body and later for turning a somewhat dried, leather, hard body. Shaping by pressing material in fired molds and firing in a closed kiln were subsequent developments [2].

The introduction of steam power in the 19th century led to the mechanization of mixing, dry pressing, filter pressing and pebble mill grinding. Near the end of 19th century, separate phases of silica were distinguished using optical microscopy, and silicon carbide was synthesized in an electric furnace. Also, pyrometric cones were developed by Seager to control firing [2].

The first half of the 20th century was seen the rapid development of x-ray techniques for the analysis of the atomic structure of crystals and later electron microscopy for evaluating microstructure beyond the limit of the optical microscope. Material systems become more refined, and special compounds were developed, synthesized, and fabricated into products for refractory and electronic applications. Then, refined organic additives were introduced to improve the processing behavior. Industrial production became mechanized, and several stages of manufacturing were automated.

Thermocouples were used to monitor temperatures during firing [2].

The second half of the 20th century has witnessed major advances in the synthesis, and fabrication of ceramic products. Scanning electron microscopy (SEM) is used for micro structural analysis for quality control after manufacturing. Several different instrumented techniques have been developed for bulk chemical analysis at a concentration of less than a fraction of one part in a million and surface concentrations a few atomic layers in thicknesses. The particle size distributions of a material can be determined to below 0.1 μm in a short time. By using a multicomponent system of additives, the flow behavior during forming is developed and controlled. Testing apparatus and processing machinery are more advanced. Computers are also used in the industry to monitor and/or control raw-material handling and preparation, fabrication, and firing [2].

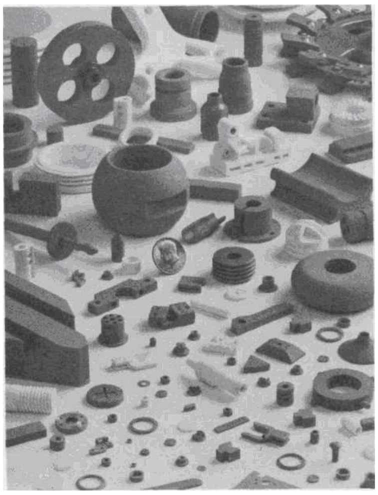

Figure 1.1. Advanced alumina structural ceramics used in a wide variety of materials-processing technology applications (textile guides, valve seals, impellers, nozzle inserts, wear blocks, cutting tools, milling media, refractory insulation supports) and electrical applications (spark plug insulators, electronic substrates, electrical insulation) [2]

Figure 1.2. Corrosion/erosion-resistant silicon carbide structural ceramic component used in the chemical processing industry [2]

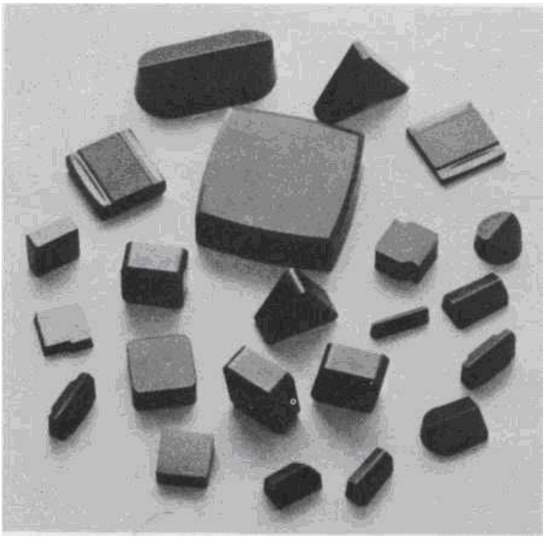

Figure 1.3. Silicon nitride metal cutting tools [2]

Table 1.1. Products Produced by Ceramic Powder Processing [2]

Electronics
Substrates, chip carriers, electronic packaging
Capacitors, inductors, resistors, electrical insulation
Transducers, servisors, electrodes, igniters
Motor magnets, spark plug insulators Advanced structural materials
Cutting tools, wear-resistant inserts
Engine components
Resistant coatings
Dental and orthopedic prostheses
High-efficiency lamps Chemical processing components
Ion exchange media
Emission control components
Catalyst supports
Liquid and gas filters Refractory structures
Refractory lining in furnaces, thermal insulations, kiln furniture
Recuperators, regenerators
Crucibles, metal-processing materials, filters, molds
Heating elements Construction materials
Tile, structural clay products
Cement, concrete Institutional and domestic products
Cookware
Hotel china and dinnerware
Bathroom fixtures
Decorative fixtures and household items

Table 1.2. Classification of Ceramics by Function [3]

Function	Class	Nominal Composition
Electrical	Insulation	$\alpha - Al_2O_3, MgO$, porcelain
	Ferroelectrics	$BaTiO_3, SrTiO_3$
	Piezoelectric	$PbZr_0.5Ti_0.5O_3$
	Fast ion conduction	$\beta - Al_2O_3$, doped ZrO_2
	Superconductors	$Ba_2YCu_3O_7 - x$
Magnetic	Soft ferrite	$Mn_0.4Zn_{0.6}Fe_2O_4$
	Hard ferrite	$BaFe_{12}O_{19}$, SrFe12O19
Nuclear	Fuel	$UO_2, UO_2 - PuO_2$
	Cladding / shielding	SiC, B_4C
Optical	Transparent envelope	$\alpha - Al_2O_3, MgAl_2O_4$
	Light memory	$dopedPbZr_{0.5}, Ti_{0.5}, O_3$
	Colors	$dopedZrSiO_4, dopedZrO_2, dopedA1_2O_3$
Mechanical	Structural refractory	$\alpha - Al_2O_3, MgO, SiC, Si_3N_4, A1_6Si_2O_{13}$
	Wear resistance	$\alpha - Al_2O_3, ZrO_2, SiC, Si_3N_4, toughenedA1_2O_3$
	Cutting	$\alpha - Al_2O_3, ZrO_2, TiC, Si_3N_4, SIALON$
	Abrasive	$\alpha - Al_2O_3, SiC, , toughenedA1_2O_3, SIALON$
	Construction	$Al_2O_3 - SiO_2, CaO - Al_2O_3, -SiO_2, porcelain$
Thermal	Insulation	$\alpha - Al_2O_3, ZrO_2, Al_6Si_2O_{13}, SiO_2$
	Radiator	ZrO_2, TiO_2
Chemical	Gas sensor	$ZnO, ZrO_2, SnO_2, Fe_2O_3$
	Catalyst carrier	$Mg_2Al_4Si_5O_{18}, A1_2O_3$
	Electrodes	TiO_2, TiB_2, SnO_2, ZnO
	Filters	$SiO_2, \alpha - Al_2O_3$
	Coatings	$NaO - CaO - Al_2O_3 - SiO_2$
Biological	Structural prostheses	$\alpha - Al_2O_3, porcelain$
	Cements	$CaHPO_4 - 2H_2O$
Aesthetic	Pottery, artware	Whiteware, porcelain
	Tile, concrete	Whiteware, $CaO - SiO_2 - H_2O$

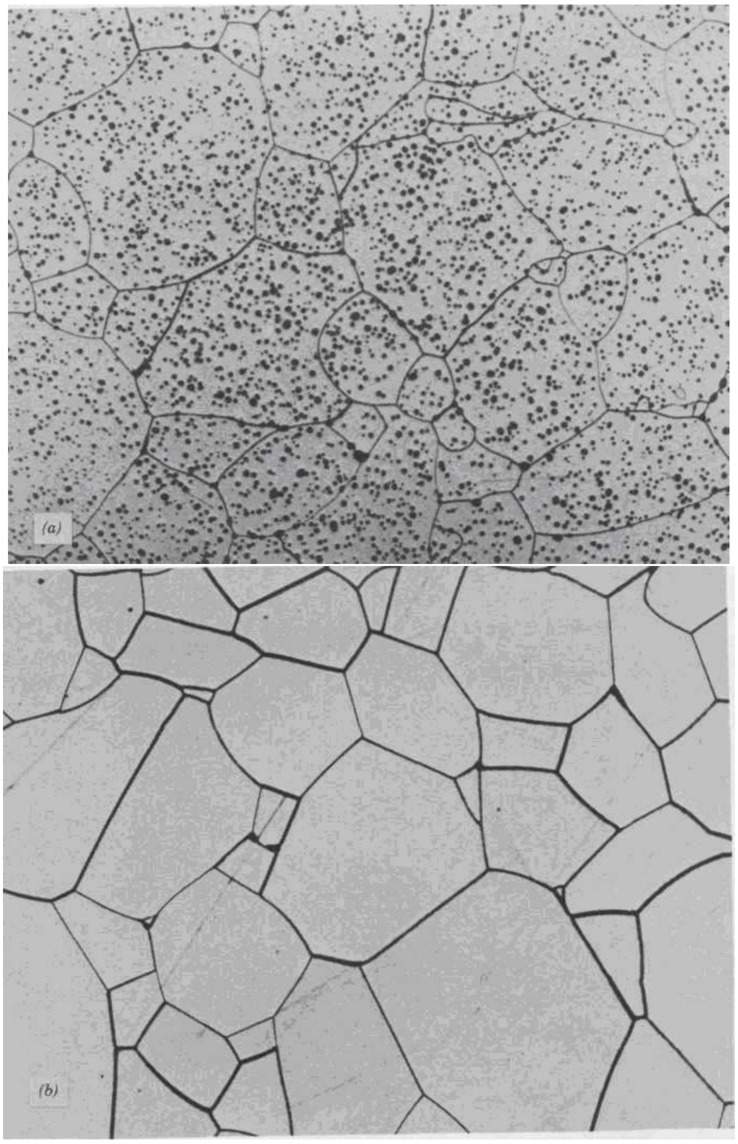

Figure 1.4. Comparative microstructures in (a) a conventional dense alumina of 98% density, (b) an optically transparent alumina exceeding 99.9% density [2]

2. TYPES OF CERAMICS

There are many ceramics at available properties. For example, alumina is available in many densities, silicon carbide in many qualities. The structure insensitive properties (density, modulus and melting point) depend little on quality - they do not vary by more than % 10. But the structure sensitive properties (fracture toughness, modulus of rupture and some thermal properties including expansion) are more variable. For these, it is essential to consult manufacturers' data sheets or conduct our own tests [1].

2.1. Vitreous Ceramics

Modern pottery, porcelain, structural and refractory bricks are made by processes which are automated, differ very little from those of 2000 years ago. All are made from clays, which are formed in the wet, and then dried, and finally fired. After firing process, they consist of crystalline phases (mostly silicates) held together by a glassy phase based, as always, on silica (SiO_2). The glassy phase forms and melts when the clay is fired, and spreads around the surface of the inert, crystalline phases, bonding them together. The important information for generic vitreous ceramics is summarized in Table 2.1 [1].

Table 2.1. Generic vitreous ceramics [1]

Ceramic	Typical Composition	Typical Uses
Porcelain	Made from Clays: Hydrous	Electrical Insulators
China	aluminum-slicate such as	Artware and
Pottery	$Al_2(Si_2O_5)(OH)_4$ mixed with	tableware tiles
Brick	other inert minerals	Construction, refractory uses

2.2. High-performance Engineering Ceramics

Diamond is the ultimate engineering ceramic; it has for many years been used for cutting tools, dies, rock drills, and as an abrasive. But, it is really expensive.

The strength of a ceramic is largely determined by two characteristics: its toughness (K_{IC}), and the size distribution of micro cracks it contains. A new class of fully dense, high-strength ceramics is now emerging which combine a higher K_{IC} with a narrower distribution of smaller micro cracks, giving properties which make them competitive with metals, even with diamond, for cutting tools, implants and engine parts. And as an advantage, they are cheap. The most important generic high-performance ceramics are listed in Table 2.2 [1].

Table 2.2. Generic high-performance ceramics [1]

Ceramic	Typical Composition	Typical Uses
Dense Alumina	Al_2O_3	Cutting tools, dies; wear resistant
Silicon carbide, nitride	SiC, Si_3N_4	surfaces, bearings; medical implants
Sialons	e.g. Si_2AlON_3	engine and turbine parts; armour.
Cubic zirconia	ZrO_2+5 wt % MgO	

2.3. Natural Ceramics

Stone is the oldest of all construction materials and also the most durable one. Stone used in a load-bearing capacity behaves like other ceramics; and the criteria used in design with stone are the same. The mechanical properties are of primary importance in some major engineering problems. Table 2.3 lists the important generic natural ceramics [1].

Table 2.3. Generic natural ceramics [1]

Ceramic	Composition	Typical Uses
Limestone (marble)	largely $CaCO_3$	
Sandstone	largely SiO_2	Building foundations, construction.
Granite	Aluminium silicates	
Ice	H_2O	Arctic engineering

2.4. Ceramic Composites

For making composites, the great stiffness and hardness of ceramics can sometimes be combined with the toughness of polymers or metals. For example, bone is a most common natural ceramic-composite: particles of hydroxyapatite (the ceramic) bonded together by collagen (a polymer). Synthetic ceramic-ceramic composites (like glass fibers in cement, or silicon carbide fibers in silicon carbide) are now under development and may have important high-temperature application in the next decade. The examples are summarized in Table 2.4 [1].

Table 2.4. Ceramic composites [1]

Ceramic composite	Components	Typical Uses
Fibre glass	Glass-polymer	High-performance structures.
CFRP	Carbon-polymer	
Cermet	Tungsten carbide-cobalt	Cutting tools, dies.
Bone	Hydroxyapatite-collagen	Main structural material of animals.
New ceramic composites	Alumina-silicon carbide	High temperature and high toughness applications.

3. STRUCTURE OF CERAMICS

A ceramic has structure at the atomic scale: its crystal structure (if it is crystalline), or its amorphous structure (if it is glassy). It has structure at a larger scale too: the shape and arrangement of its grains or phases; the size and volume fraction of pores it contains. Ceramic structures differ from those of metals. Their complex details (and they can be pretty complex) are the province of the professional ceramist; but we need a working knowledge of their basic features to understand the processing and the engineering uses of ceramics and to appreciate the recently developed high-strength ceramics [1].

Crystalline ceramics form polycrystalline microstructures, like those of metals. Grains are more or less perfect crystals, meeting their neighbors at grain boundaries. The structure of ceramic grain boundaries is obviously more complicated than those in metals: ions with the same sign of charge must still avoid each other and also, valency requirements must be met in the boundary, just as they are within the grains. In addition, none of this is visible at the micro structural level, which for a pure, dense ceramic [1].

Many ceramics are not fully dense. The common features of the microstructure are porosities as high as 20 %. The material are weaken by the pores, though if they are well rounded, the stress concentration they induce is small. More damaging are cracks; they are much harder to see, but they are nonetheless present in most ceramics, left by processing, or nucleated by differences in thermal expansion or modulus between grains or phases. These eventually determine the strength of the material. Recent developments in ceramic processing aim to reduce the size and number of these cracks and pores, giving ceramic bodies with tensile strengths as high as those of high-strength steel [1].

Ionic ceramics are, typically, compounds of a metal with a non-metal; sodium chloride, NaCl; magnesium oxide, MgO; alumina, Al_2O_3; zirconia, ZrO_2. The metal and nonmetal have unlike electric charges: in sodium chloride, for instance, the sodium atoms have one positive charge and the chlorine atoms have one negative charge each. The most of the bonding are given by the electrostatic attraction between the unlike charges. So the ions pack densely (to get as many plus and minus charges close to each other as possible), but with the constraint that ions of the same type (and so with the same charge) must not touch [1].

Covalent ceramics are different. They are compounds of two non-metals (like silica, SiO_2), or just pure elements (like diamond, C, or silicon, Si). An atom in this class of ceramic bonds by sharing electrons with its neighbours gives a fixed number of directional bonds. Often these are non-crystalline; as an example, all commercial glasses are three-dimensional amorphous networks based on silica, SiO_2 [1].

4. MECHANICAL PROPERTIES OF CERAMICS

Ceramics have generally a well-defined Young's modulus: the value does not depend significantly on loading time (or, if the loading is cyclic, on frequency). By reflecting the greater stiffness of the ionic bond in simple oxides, and of the covalent bond in silicates, ceramic moduli are generally larger than those of metals. Since, ceramics are largely composed of light atoms (oxygen, carbon, silicon, aluminium) and their structures are often not close-packed, their densities are low. Because of this property, their specific moduli (E/ρ) are attractively high. Table 4.1 shows that alumina, for instance, has a specific modulus of 100 (compared to 27 for steel) [1].

Table 4.1. Specific moduli ceramics compared to metals [1]

Material	Modulus E (GPa)	Density ρ (Mgm^{-3})	Specific modulus E/ρ (GPa/Mgm^{-3})
Steels	210	7.8	27
Al alloys	70	2.7	26
Alumina, Al_2O_3	390	3.9	100
Silica, SiO_2	69	2.6	27
Cement	45	2.4	19

Ceramics are really the hardest of solids. Corundum (Al_2O_3), silicon carbide (SiC) and, of course, diamond (C) are used as abrasives: they will cut, or grind, or polish almost anything, even glass, and as it is well known that glass is itself a very hard solid. When a material yields in a tensile test, or when a hardness indenter is pressed into it, dislocations move through its structure. Each test, in its own way, measures the difficulty of moving dislocations in the material. Metals are inherently soft. Because of the ionic or covalent bonds presenting an enormous lattice resistance to the motion of a dislocation, most of the ceramics are inherently hard [1].

Brittleness is the penalty that must be paid for choosing a material with a large lattice resistance, the fracture toughness is low. The lattice resistance makes slip very difficult even at the tip of a crack, where the stress is intensified. It is defined as the crack-tip plasticity which gives metals their high toughness: energy is absorbed in the plastic zone, making the propagation of the crack much more difficult. Although some plasticity can occur at the tip of a crack in a ceramic too, it is very limited; the energy absorbed is small and the fracture toughness is low [1].

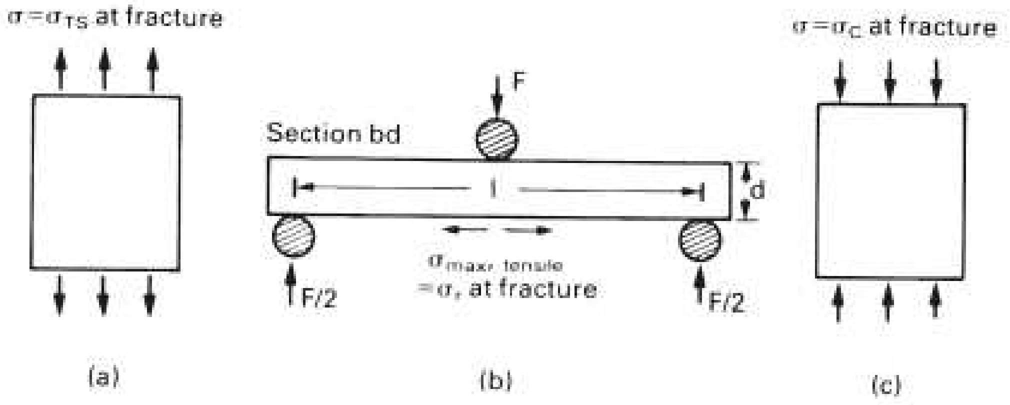

Figure 4.1. Tests which measure the fracture strengths of ceramics (a) The tensile test measures the tensile strength (b) The bend test measures the modulus of rupture (c) The compression test measures the crushing strength [1]

Ceramics have values of the fracture toughness (K_{IC}) which are roughly one-fiftieth of those of good, ductile metals. In addition, they always contain cracks and flaws. The cracks originate in several ways. Most generally the production method leaves small holes: sintered products, for instance, generally contain angular pores on the scale of the powder (or grain) size. And thermal stresses caused by cooling or thermal cycling can generate small cracks. Even if there are no processing or thermal cracks, corrosion (often by water) or abrasion (by dust) is sufficient to create cracks in the surface of any ceramic material. If they do not form any other way, cracks appear during the loading of a brittle solid, nucleated by the elastic anisotropy of the grains, or by easy slip on a single slip system. The design strength of a ceramic, then, is determined by its low fracture toughness (K_{IC}), and by the lengths of the micro cracks it contains. If the longest micro crack in a given sample has length $2a_m$, then the tensile strength is simply:

$$\sigma_{TS} = \frac{K_{IC}}{\sqrt{\pi a_m}} \tag{4.1}$$

where K_{IC} is the fracture toughness [1].

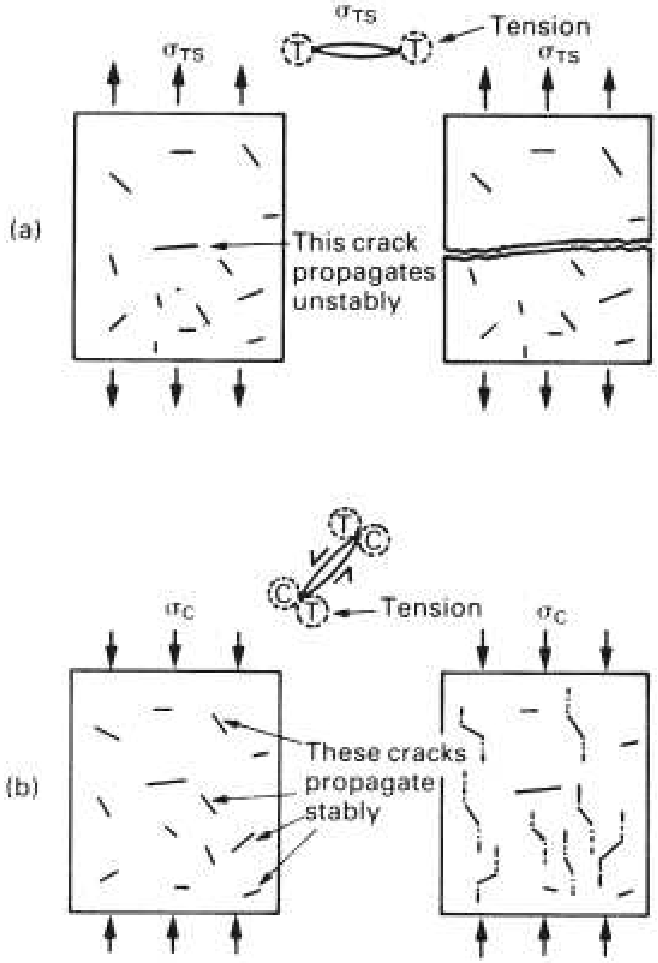

Figure 4.2. (a) In tension the largest flaw propagates unstably (b) In compression, many flaws propagate stably to give general crushing [1]

As it is seen that, there are two ways of improving the strength of ceramics: decreasing a_m by careful quality control, and increasing K_{IC} by alloying, or by making the ceramic into a composite. But first, we must examine how strength is measured. The common tests are shown in Figure 4.2. The obvious one is the simple tensile test (Figure 4.2 (a)). It measures the stress required to make the longest crack in the sample propagate unstably in the way. But it is hard to do tensile tests on ceramics, because they tend to break in the grips. It is much easier to measure the force required to break a beam in bending. The maximum tensile stress in the surface of a beam when it breaks is called the modulus of rupture, σ_r; for an elastic beam it is related to the maximum moment in the beam, M$_r$, by;

$$\sigma_r = \frac{6M_r}{bd^2} \tag{4.2}$$

where d is the depth and b the width of the beam. It is thought that σ_r should be equal to the tensile strength σ_{TS}. But it is actually a little larger (typically 1.7 times larger) [1].

The third test is the compression test. For metals (or any plastic solid) the strength measured in compression is the same as that measured in tension. But for brittle solids this is not so; for these, the compressive strength is roughly 15 times larger, with $\sigma_C \approx 15\sigma_{TS}$. Crack in compression propagates stably, and twist out of their original orientation to propagate parallel to the compression axis. Fracture is not only caused by the rapid unstable propagation of one crack, but the slow extension of many cracks to form a crushed zone. It is not the size of the largest crack (a_m) that counts, but that of the average a. The compressive strength is still given by a formula;

$$\sigma_C = C\frac{K_{IC}}{\sqrt{\pi\overline{a}}} \tag{4.3}$$

but the constant C is about 15, instead of 1 [1].

Fracture caused by sudden changes in temperature is a problem with ceramics. One way of measuring thermal shock resistance is to drop a piece of the ceramic, heated to progressively higher temperatures, into cold water. The maximum temperature drop $\triangle T$ (in K) which it can survive is a measure of its thermal shock resistance. If its coefficient of expansion is α then the quenched surface layer suffers a shrinkage strain of $\triangle T$. But it is part of a much larger body which is still hot, and this constrains it to its original dimensions: it then carries an elastic tensile stress $E\triangle T$. If this tensile stress exceeds that for tensile fracture, σ_{TS}, the surface of the component will crack and eventually spall off. So the maximum temperature drop $\triangle T$ is given by;

$$E\alpha\triangle T = \sigma_{TS} \tag{4.4}$$

For most of the high-performance engineering ceramics, α is small and σ_{TS} is large, so they can be quenched suddenly through several hundred degrees without fracturing [1].

The Swedish engineer, Weibull, invented the following way of handling the statistics of strength. He defined the survival probability $P_S(V_0)$ as the fraction of identical samples, each of volume V_0, which survive loading to a tensile stress σ. He then proposed that;

$$P_S(V_0) = exp\left\{-\left(\frac{\sigma}{\sigma_0}\right)^m\right\} \tag{4.5}$$

where σ_0 and m are constants. The constant m, it is called the Weibull modulus, tells us that how rapidly the strength falls as we approach σ_0. The lower m means the greater the variability of strength. The engineering ceramics (e.g. SiC, Al_2O_3 and Si_3N_4) have values of m of about 10 [1].

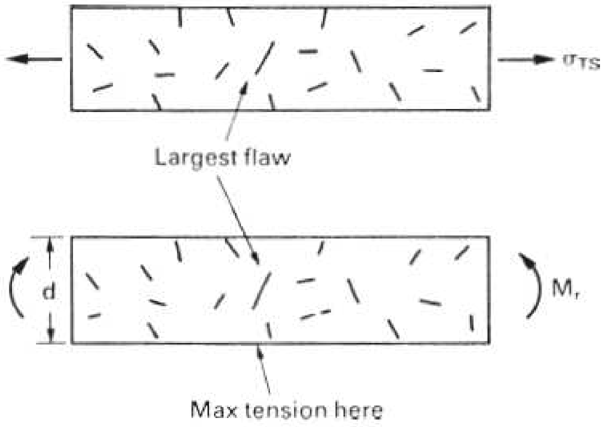

Figure 4.3. Ceramics appear to be stronger in bending than in tension because the largest flaw may not be near the surface [1]

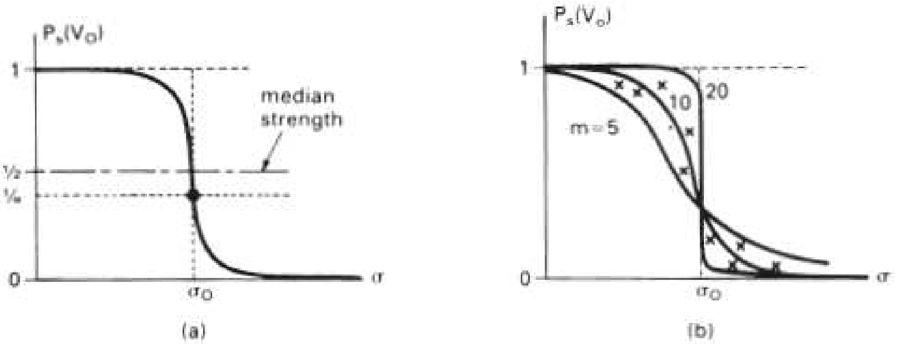

Figure 4.4. (a) The Weibull distribution function (b) When the modulus, m, changes, the survival probability changes as shown [1]

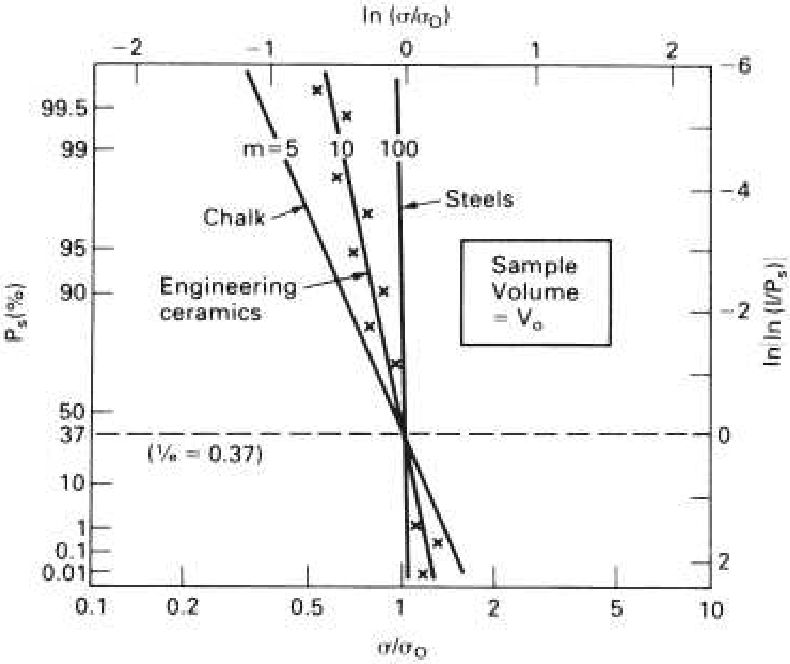

Figure 4.5. Survival probability plotted on “Weibull probability” axes for samples of volume V_0 [1]

5. INDUSTRIAL CERAMIC PROCESSING

Ceramic processing commonly begins with one or more ceramic materials, one or more liquids, and also one or more special additives called processing aids. The starting materials or the batched system may be beneficiated chemically and physically using operations such as crushing, milling, washing, chemical dissolving, settling, flotation, magnetic separation, dispersion, mixing, classification, de-airing, filtration, and spray-drying. The forming technique used depends on the consistency of the system (i.e., slurry, paste, plastic body, or a granular material) and produces a particular unfired shape with a particular composition and microstructure. Drying process removes some or all of the residual processing liquids. Additional operations may be followed with green machining, surface grinding, surface smoothing and cleaning, and the application of surface coatings such as electronic materials or glaze. The finished material is then commonly heat-treated to produce a sintered microstructure. The sintered product may be a single component or a multi-component composite structure [2].

The objectives of the ceramic processing science are to identify the important characteristics of the system and also understand the effects of processing variables on the evolution of these characteristics. The objectives in process engineering should be to change these characteristics purposefully to improve product quality. Because of the key dependence on controlling characteristics, an understanding of techniques for characterizing the starting material and process system at each stage is an integral part of any discussion of ceramic processing. Raw materials are now more beneficiated, more consistent, and often much simpler in composition. Modern instrumentation for analyzing ceramics materials and systems is more automated, precise, and with microcomputer accessories quantitative data are obtained and presented in a convenient format [2].

5.1. Slip Casting

Slip casting is an economical process which is extensively used to produce complex shapes from a broad range of ceramic-based materials [25-30, 38]. Applications are numerous, including art ware, chinaware, sanitary ware, crucibles, filter media, structural tubing, bone implants, and heat engine components [4].

A slip is described as a suspension of colloidal powders in a liquid (usually water). Slip casting entails pouring the slip into a permeable mold (usually gypsum). Capillary suction of the mold causes the liquid to be filtered from the suspending medium and a densely packed layer of particles to be deposited against the mold wall. This process is shown in Figure 5.1 [4].

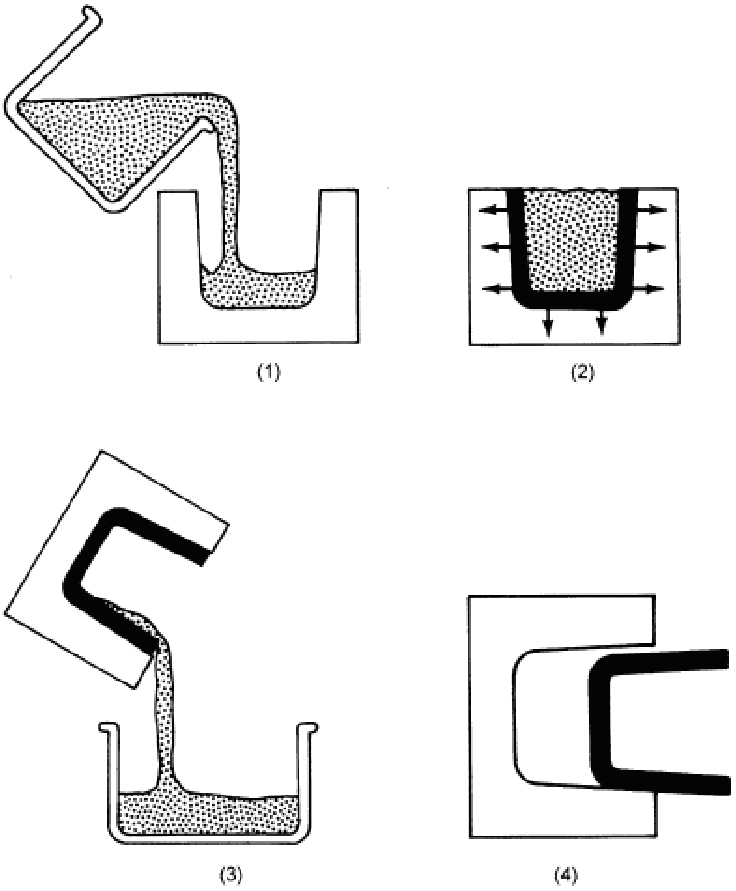

Figure 5.1. Slip casting illustration, (1) Permeable mold is filled with slip (2) Liquid is extracted from the mold, while forming compacts along mold walls (3) Excess slip is drained (4) Casting is removed after partial drying [27]

Slip casting has been used widely by ceramists to form green bodies that can be fired to produce articles, ranging from the most delicate pottery to the household toilet. Chemical engineers, on the other hand, have been using pressure filtration to remove unwanted solids from liquids (or vice versa). The ”green body” formed by the chemical engineer is called a filter cake and is frequently discarded as waste. Despite these different results, the ceramists and chemical engineers share common goals in their processes, namely maximizing green density (minimizing water content in the cake) and also maximizing casting (filtration) rate [4, 49].

Many slip casting variations are used, depending on the application requirements. Drain casting, the mostly used process, involves casting for a limited time period to deposit a layer of the desired thickness. The remaining slip is subsequently drained from the mold cavity. Another common process is known as solid casting, which is identical to drain casting except that slip is continually added until a solid case is made. Pressure filtration entails pressurizing the slip to increase the casting rate. A less common approach is known as vacuum casting, in which a vacuum is applied to the outside of a mold. This process can be used to increase casting rates with either the drain or solid casting approach [4].

Centrifugal casting is a relatively new process in which the spinning of a mold produces large forces that serve to increase consolidation rates [4, 6, 7].

The production of complex shapes can be accomplished by slip casting, using insoluble mandrels attached to a mold. One example is fugitive wax slip casting, which is based on the much older technology of investment casting [4, 9, 27].

The process of slip casting ceramics has traditionally involved pouring a dispersion of fine particles (usually clay) into a porous (plaster of paris) mold. The capillary suction pressure pulls water into the pores of the mold leaving behind a deposit of the particles and water. In the chemical industry, filtration to remove unwanted solids from liquids has involved applying an external pressure to the slurry to drive water through a permeable medium upon which the wet deposit (filter cake) forms. The driving forces include the use of hydraulic rams, pressure, vacuum, and centrifugal forces. Slip casting is a case of filtration where a desired shape is formed using capillary pressure as the traditional driving force [5].

Table 5.1. Examples of compositions of casting slurries [2]

Whiteware Slip			Refractory Slip	
Material	Concentration (vol %)		Material	Concentration (vol %)
Nonplastics	25-30		Alumina (¡45 μm)	40-50
Clay	15-25		Ball Clay	0-10
Water	45-60		Water	50-60
		Additives* (wt %)		
Na_2SiO_3				
Na polyacrylate				
Na lignosulfonate	< 0.5	Deflocculant	NH_4 polyacrylate	0.5-2
$CaCO_3$	< 0.1	Coagulant	$MgSO_4$	0-0.1
$BaCO_3$	< 0.1			
Clay $< 1\mu m$	Variable amount	Binder	NH_4 alginate	0-10
			carboxymethyl-cellulose	0-10
			methyl cellulose	
			hydroxyethyl-cellulose	0-0.5

* Percentage of weight of solids in slurry

5.1.1. Surface Chemistry and Rheology

In many ceramic shaping processes, the dispersion of the ceramic powder in an aqueous medium is required. These aqueous suspensions (slurries) have to fulfill several requirements. For example, the particles should not settle fast under the effect of gravity, they should be able to remain in suspension, otherwise segregation occurs which causes density inhomogeneities in the cast objects. In addition, the slurries have to be easily reproduced and be insensitive to slight variations in solid content and storage time. They also have to be of high solid content, in one hand to achieve reasonable casting rates and on the other hand to reduce energy consumption in the subsequent drying stage due to the lower moisture content to be removed [4, 56].

Particle surface chemistry is an important factor in the slip casting process, because it regulates interparticle attraction and repulsion forces, which have significant effects on slip rheology, casting rate, and microstructure evolution [10-14]. The control of surface chemistry while preparing low-viscosity suspensions that are highly concentrated with powders is a significant requirement of slip casting. Low viscosities (<1 Pa.s) are needed for pourability, and high solid concentrations (up to 60 vol % solids) are needed to maximize the casting rate and "green" density as well. Traditional methods for maintaining low-viscosity, concentrated suspensions entail the use of polydisperse particle size systems and repulsive interparticle forces that arise from surface-adsorbed ions or polymers [11]. Low-viscosity, highly concentrated suspensions can also be formed by the use of attractive forces between particles that are coated with lubricating polymers [4, 11, 15].

Regulating surface forces by altering the slip chemistry is also fundamental for eliminating cast layer heterogeneities such as size-segregation of particles, large isolated pores and spatial variations of packing density. These defects can create fracture origins in fully sintered ceramics, and can cause cracks during drying and sintering because of no uniform shrinkage stresses [4].

5.1.2. Surface Forces and Rheology

A common trend in ceramic processing is the development of smaller powders (<1 μm) in order both to enhance sintering rates, and to reduce the size scale for mixing uniformity in powder blends. For example, slip casting of advanced composites using very fine particles can produce unique properties resulting from the submicrometer-scale architecture of the component phases [16-19, 28]. A concern with the use of submicrometer-sized powders is spontaneous agglomeration resulting from the coupling of electronic oscillations of the atoms in adjacent particles (Van der Waals-London attraction). Ceramic particles generally contain atoms that are easily polarizable. Thus, it creates a strong interparticle attraction. Agglomerates defeat the purpose of reducing the scale of mixing. They also can produce spatial variations of packing density that lead to cracking and impaired mechanical properties [4].

A suggested approach for eliminating agglomerates is to establish interparticle repulsion forces by mixing powders in a liquid with dissolved ions or polymers, which then adsorb to the particle surfaces [2, 14-24, 25-28]. The former technique (electrostatic stabilization) is mostly used in slip casting process and entails spontaneous formation of a "diffuse double layer" of dissolved ions surrounding each particle due to the presence of oppositely charged surface sites. The latter method involves adding either neutral (steric stabilization) or charged (electrosteric stabilization) polymers to a suspension [4].

Rheological properties and slip cast micro structures can be produced from a given powder using the stabilization techniques. Generally, interparticle repulsion results in dispersed slurries that exhibit Newtonian rheology viscosity is independent of shear rate at the low particle concentrations. At high solid concentrations, the slurries become dilatant (viscosity increases with shear rate), because the volume must increase upon shearing to allow closely spaced particles to slip past one another. Dispersed slips generally result in the slow casting of densely packed microstructures that have low permeability. In contrast, attractive interparticle forces result in flocculated slips which become exceedingly viscous above 10 to 20 vol % solids unless lubricating adlayers are present [4, 15].

Generally, flocculated slips exhibit pseudoplastic thixotropic rheology (viscosity decreases with increasing shear rate). Casting rates are usually rapid, because the microstructures are typically permeable and porous. After stirring, these slips may exhibit increased viscosity as a result of time-dependent agglomeration (rheopexy) [4].

5.1.3. Electrostatic Stabilization

When suspended in aqueous media, particles carry a surface charge that is balanced by counter-ions in solution. With most of clays, the surface charge arises from a valence deficiency resulting from isomorphous substitution in crystal lattice [30]. The surface charge results from the ionization of surface moieties with nonclay materials. For instance, oxides possess surface charges that are determined by the following surface hydroxyl reactions:

$$\text{M-OH}^0 + \text{H}^- = \text{M-OH}_2^- \tag{5.1}$$

$$\text{M-OH}^0 = \text{M-O}^- + \text{H}^- \tag{5.2}$$

where M denotes a surface cation, such as Al or Si [31-33]. The net surface charge depends on the solution pH, which describes the relative concentrations of potential-determining ions (H^+ and OH^-) in the solution. A net positive or negative charge occurs at low pH and high pH based on the above reactions, respectively. The isoelectric point is the pH at which the net surface charge is approximately zero. Potentiometric titration technique is used to measure the concentration of potential determining ions adsorbed to particle surfaces [4, 34].

At a given pH, the net surface charge also depends on the valence and population density of the surface cations that are bonded to hydroxyls. Parks and de Bruyn [31] reported an empirical relationship for estimating the isoelectric point of oxide ceramics based on this consideration. This relationship states that decreases in the isoelectric point are linearly proportional to the ratio Z/R, where Z and R equal the cation valence and radius, respectively (in general, the smaller the number of surrounding oxygen atoms and the greater the number of cation sites per unit area) [4]. Extensive tabulations of isoelectric points are reported before by Parks and de Bruyn [31] and James [35].

There is not any good quantitative theory to explain the dispersion and rheology of concentrated suspensions; however, there are well-developed theories on the surface forces between two particles [21, 23, 32-37].

5.1.4. Slip Control

Constancy of slip and mold properties is essential for achieving rheological properties, casting rate, settling rate, drain properties, mold-release properties, drying shrinkage and green strength. The slip must be easily reproduced and should be insensitive to slight variations in solids content, mixing conditions, chemical composition and storage time. The viscosity must be low enough to allow complete filling of the mold, but the solids content must be high enough to achieve a reasonable casting rate. The empirical methods are traditionally used to determine optimum conditions. The slip must also be free of air bubbles (or chemical reactions producing bubbles) that may become critical defects in the sintered body. Slips are generally aged to keep properties consistent, and then final viscosity measurements are performed before deairing and casting [4].

The selection of additives, particularly for those methods employing a high concentration of additives, is an important step in the forming process. And, an understanding of the chemical, mechanical and rheological properties of the additives is important for the forming step. Because in almost all practical systems, the additives must be removed prior to densification of the body during the firing step, the thermal decomposition characteristics are also important [4, 53, 54].

Organic polymers are common slip ingredients that serve in a number of functions, such as dispersants, viscosity modifiers, plasticizers, and binders (in reference to their utility for improving green-body strength). Aqueous suspending media are used to dissolve these polymers, although various organic solvents can be used (such as alkanes or alcohols) [4].

Binders are usually 10,000 to 30,000 molecular weight polymers such as acrylics (for example, polyacrylic acid or polymethacrylic acid), vinyls (for example, polyvinyl alcohol), alginates, and various cellulose-based polymers. Plasticizers are typically small to medium-sized molecules that decrease cross-linking among binder molecules and make castings more pliable (for example, polyethylene glycol or butyl benzyl phthalate) [4]. Extensive reviews of organic polymers and their effects on slurry rheology are presented before by several authors [2, 26, 30].

A concern with the use of organic polymers is that they are transported into the capillaries of the molds and may be difficult to remove. This can change the mold suction behavior, permeability, and shorten the life of the mold. The use of organic chemicals may also cause health hazards. There are some concerns associated with the burn-out of organics, such as the production of toxic gases and the formation of carbonaceous residues in sintered microstructures [4, 28].

It is essential to control the particle size distribution in order to maximize the packing density of a cast layer and thereby minimize dimensional shrinkages during drying and sintering process [2, 29, 30]. Several packing models are available to aid in formulating mixtures of different-sized particles to obtain maximum packing efficiency [2, 30]. Various size fractionation methods can be used to alter the particle size distribution, such as sieving, air classification, centrifugation and sedimentation. Additionally, comminution techniques (for example, milling or crushing) are used to pulverize agglomerates and reduce the average particle size. Particle size distribution measurements are easily measured by a variety of methods, including sieving, optical and electron microscopy, x-ray absorption, light scattering, light intensity fluctuation, and electrical sensing [2, 4, 30].

Another reason for controlling particle size distribution is to eliminate microstructure heterogeneities, such as large particles and hard agglomerates. For instance, the sedimentation of heavy particles or hard agglomerates during casting can result in thickness and density variations, which may lead to defects in greenware and cracking during drying or sintering. It is preferred to prepare slips with repulsive interparticle forces to break apart weak agglomerates, fractionate inclusions greater than a given size, and mix different fractionated powders. Once dispersed, fractionated and mixed suspensions can be subsequently cast or the interparticle forces can be made attractive in order to form a low density deformable network that prevents mass segregation.

Another approach to minimize segregation of heavy particles or agglomerates is to increase the solids content of a dispersed slip, which increases the casting rate [4].

Proper control and characterization of slip rheology is perhaps the most important parameter in slip casting [30]. Rheological properties are not only dependent on interparticle forces, but also depend strongly on the particle size and concentration. In general, the viscosity increases with smaller particles and higher solids concentrations, because of increased particle-particle interactions. For the same reason, reduced viscosities generally result at a given solids concentration, when spherical particles are used to instead of platelets or rods [4].

Characterization of slips generally entails measurements of shear stress and viscosity as a function of shear rate over a range of shear rates of 1 to 10 s^{-1}. An important aspect of dense-packed colloidal structures in slip-cast layers is the ability to store and dissipate energy upon deformation (viscoelasticity). A full characterization of dense-packed networks can be obtained using experimental procedures such as stress growth, forced oscillation, stress relaxation, or creep compliance. There are several references on the rheology of ceramic suspensions [2, 4, 14, 20, 25, 26, 30, 37, 38, 39, 40].

Once casting is completed, a given part begins to dry and shrink away from the mold. If sticking occurs, the part can be damaged and rejected. Mold release can be aided by coating the walls of the molds with a release agent such as silicone oil, olive oil, or dilute aqueous solution (5 wt %) of sodium alginate. However these coatings may alter the casting rate [4].

5.1.5. Mechanics of Slip Casting

In slip casting, a mold is commonly made from gypsum for repetitive use. The pressure at the gypsum cast boundary is approximately equal to the capillary suction pressure, P, and is approximated by the Laplace equation:

$$P = S.\sigma.\cos\gamma \tag{5.3}$$

where S is the specific surface area of gypsum, σ is the surface tension of water, and γ is the contact angle ($cos\gamma$ =1 as gypsum is completely wetted by water). Capillary suction for water in gypsum varies between 0.03 and 0.1 MPa (4.5 and 14-5 psi) [4, 29, 41].

Slip casting is generally limited to the production of thin-walled articles (= 15 mm, or 0.6 in., maximum thickness) because of casting rate limitations imposed by the hydraulic resistances of the cast and mold. The effects of process parameters on casting rates are revealed using a filtration kinetics model, which is based on an incompressible cake having a uniform cross-sectional areas as shown in Figure 5.2 [4, 42-44].

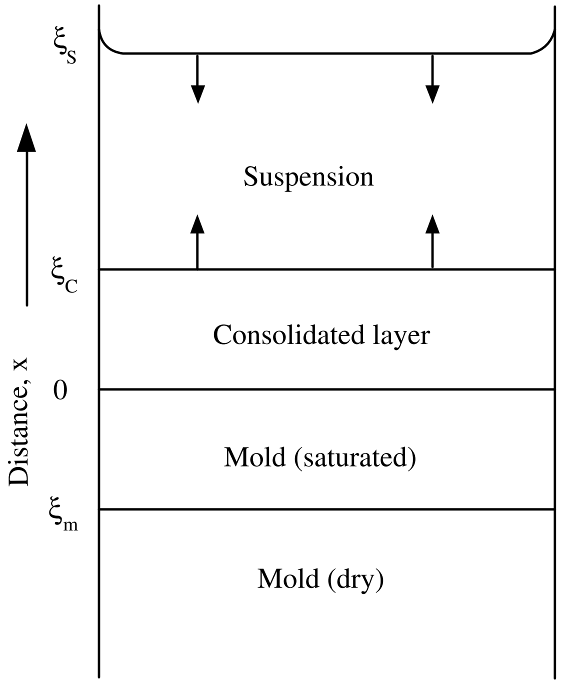

Figure 5.2. Model slip casting [44]

The model predicts that thickening rates diminish as a parabolic function of time:

$$\xi_C = \frac{\xi_S^0 - \xi_S}{n} = \frac{-\varepsilon_m . \xi_m}{n} = \left[\frac{2P.t}{n\eta\varepsilon_m(n\alpha_m + \alpha_c)} \right]^{1/2} \tag{5.4}$$

$$n = \frac{1 - c - \varepsilon_c}{c} \tag{5.5}$$

In these expressions, ξ_C is the cast layer thickness, t is time, P is the total pressure effecting filtration, ξ_S^0 is the position of the suspension-air interface at $t = 0$, ξ_S is the position of the suspension-air interface during filtration, ξ_m is the position of the filtrate air interface in the mold, η is viscosity of the suspending medium, c is the volume fraction of solids in the slip, and n is a mass balance factor. The values ε_m and ε_c are the void ratios of the mold and cast, respectively, whereas α_m and α_c are the specific hydraulic resistances (reciprocal permeabilities) of mold and cast, respectively. Above equations reveal that increases in casting rate result from decreasing α_m and α_c as well as increasing P, c, ε_m and ε_c. Gypsum molds typically have large porosities, rendering small values of α_m. The total flow resistance is usually dominated by much larger values of α_c, which result from the high packing densities of typical casts [4].

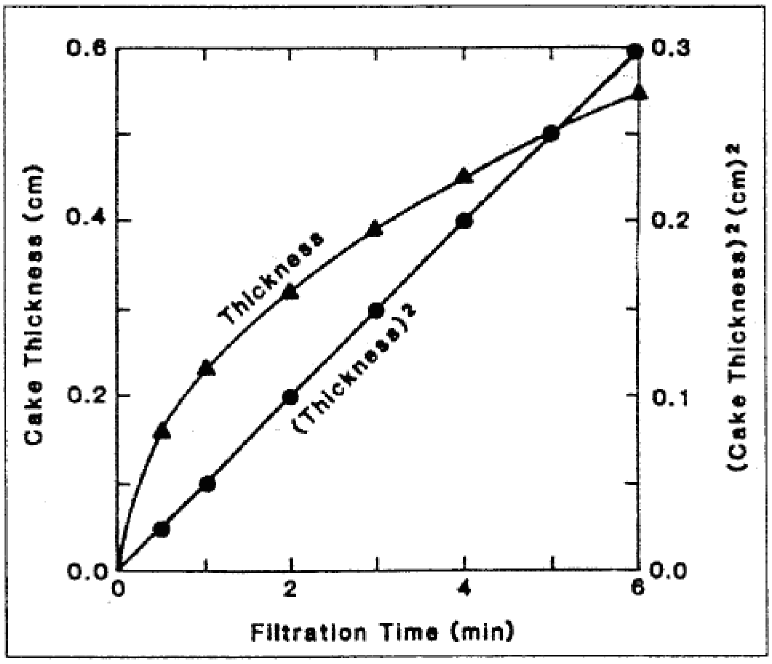

Figure 5.3. Parabolic behavior of cast thickness with time and linear dependence of cast (thickness) with time when slip casting a porcelain slip [2]

Tiller and Tsai [45] extended the above model for compressible cakes, and Hampton et al [45], modified the approach to consider transportation of fine particles. Useful information on the homogeneity of a cast layer can be obtained by correlating equation above with laboratory measurements of filtration kinetics [4, 12, 42, 44, 47].

Typical procedures entail casting a suspension of known c in an apparatus having a constant cross-sectional area; measurements of ξ_C or $(\xi_S^0 - \xi_S)$ are plotted as a function of $t^{1/2}$. A strictly linear plot is desirable, because it indicates constancy of the microstructure-related parameters in above equations and thereby suggests uniformity of the cast-layer microstructure. Possible causes of deviations from linearity and thus homogeneity are associated with either the presence of large flow units (that is hard agglomerates) that could settle to the bottom layer as sediment or with changes in α_c that may result from time-dependent flocculation of a suspension. In addition, packing densities may vary across a given cast layer due to special variations of the effective stress (that is the stress supported by the particle network) [4, 45, 48].

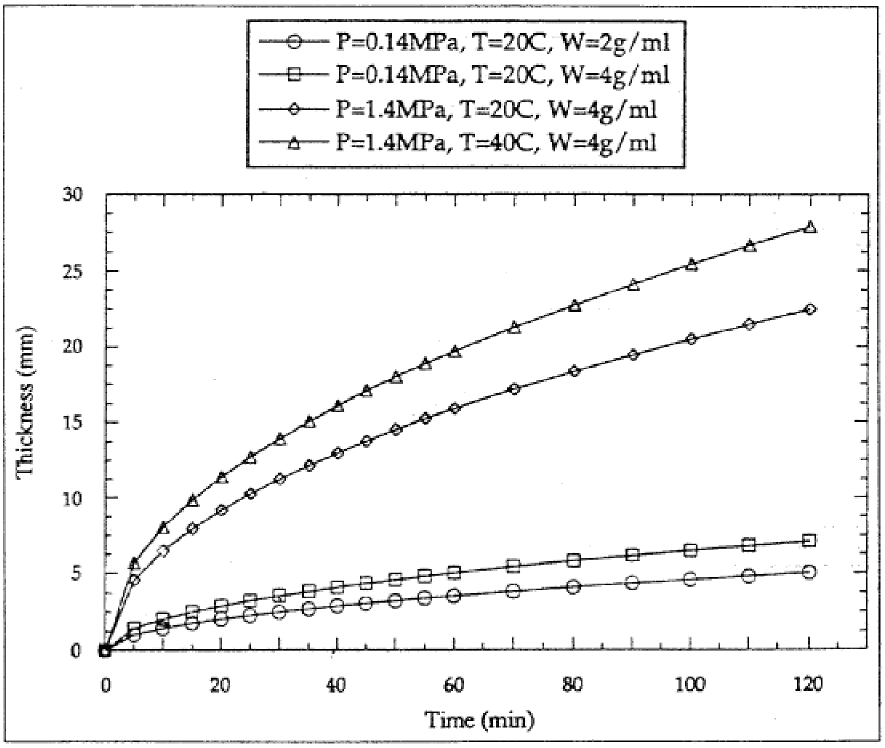

Figure 5.4. Effect of combinations of pressure, solids in slurry, and temperature on thickness of cast with time (calculated for slurry alumina powder deflocculated with polyacrylate deflocculant) [2]

Effective stresses are tpically lowest at the top of a cast layer and increase to maximum values at the bottom of he cast layer as a result of cumulative drag forces. For flocculated slips, this can result in the localized compaction of a high-density, low-permeability layer at the mold-cast layer interface [4, 45, 48].

5.1.6. Plaster (Gypsum) Mold

Permeable molds for casting are commonly gypsum with 40-50 % porosity. The casting time may range from a few minutes for a porcelain product with a thin wall to about 1 h for a thin but dense cast from a well-deflocculated slurry of fine powder or a relatively thick (2 cm), more porous cast from a partially flocculated white ware casting slip. The casting time for a dense solid cast refractory of fine particle size may range up to several weeks for thicknesses of 30 cm. Casting times are reduced significantly when using vacuum, pressure, and centrifugal casting [2].

The most commonly used permeable mold material is gypsum ($CaSO_4.2H_2O$) formed from the reaction between plaster of Paris ($Ca\ SO_4{\cdot}0.5H_2O$) and water;

$$CaSO_4.0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{5.6}$$

Gypsum is used for reasons of its relatively low cost, ability to cast molds with good surface smoothness and detail, high ultimate porosity and small pore size, short setting time, and small dimensional expansion (about 0.17 %) on setting, which aids release from models [2].

Processing of gypsum molds begins with mixing a plaster-water slurry and pouring it into a case mold having the same shape as the final greenware product. Case molds are typically made of gypsum, epoxy resin, or a combination of these materials. After filling the case mold, the slurry sets into a rigid shape via the chemical hydration of plaster ($CaSO_4.0.5H_2O$) to gypsum ($CaSO_4.2H_2O$). This process entails the nucleation and growth of needle shaped gypsum crystals which entangle and become tightly interlocked with random orientation. The final size of the gypsum crystals is approximately 2 to 5 μm (80 to 200 μin.) in diameter by up to 20 μm (800 μin.) in length. The pore spaces among these crystals interconnect in all directions to produce irregularly shaped, continuous capillaries ($\sim$ 0.1 μm or 4 μin., diameter) that are excess water. The freshly set mold is separated from the case mold and the excess water is subsequently evaporated [4].

According to Equation 5.6, the weight ratio of water to plaster required for hydration forming gypsum is 18.6/100. A range of 60/100 to 80/100 water/plaster is used in slurries for production molds. During setting, an interconnected network of needle and platelike arrangements of gypsum crystals is formed and gives the mold strength. The high water/plaster ratio used for an industrial casting mold produces the highest porosity and a slightly larger pore size, which increases the water absorption but lowers the strength. Stronger molds for pressing are prepared at a water/plaster ratio of about 40/100; air must be blown through the mold after the initial set to maintain continuous pore channels. The setting time and crystal structure in the gypsum mold depend on the temperature and electrolytes in the water and the mixing time, and these variables must be controlled to obtain molds with reproducible behavior [2].

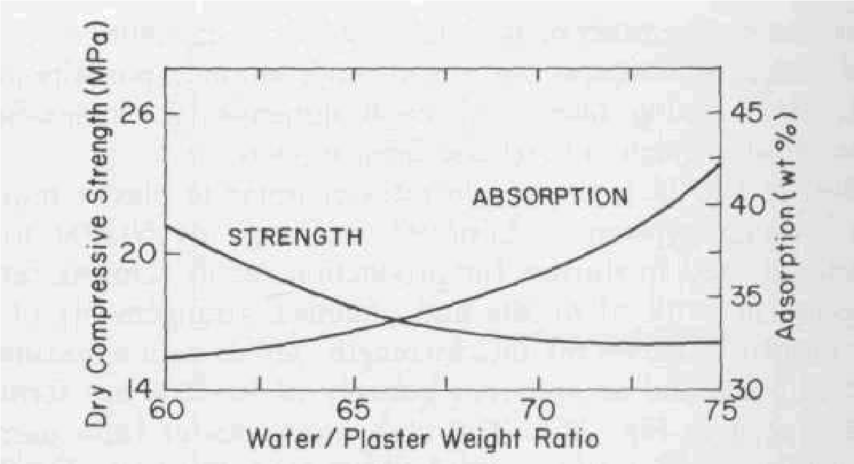

Figure 5.5. Dependence of the absorption, and compressive strength on the water/plaster ratio used in fabricating gypsum molds [2]

Disadvantages of gypsum molds are their low compressive strength when partially saturated with water, erosion in use due to their low abrasion resistance and the significant solubility of gypsum in water, their relatively low thermal shock resistance, and the potential desiccation of the gypsum when heated above 40 ^{o} C during drying, as is indicated in Table 5.2. Improved mold materials such as a porous fired ceramic, a porous polymer resin, and paper products have been developed but are not yet widely used because of difficulties in fabrication and in controlling dimensional tolerances and surface detail. The life of gypsum molds is lower when using acidic aqueous slurries or an alcohol medium. Mold coatings such as alginate, talc, and paper pulp are sometimes applied on the mold surface to facilitate separation of a cast part during drying [2].

Table 5.2. Properties of Conventional Gypsum Molds [8]

Desiccation	Dehydrates in dry air
Thermal expansion ($^0C^{-1}$)	155×10^{-7}
Compressive strength (MPa)	
Dry	14
Wet	7
Tensile strength (dry, MPa)	3
Solubility in water at $25°C(g/L)$	2.6

5.2. Pressure Slip Casting

One of the oldest forming techniques in the ceramics industry is slip casting. The casting of clay articles in porous plaster molds has been used for centuries to form a wide variety of articles. The major drawback to the slip-casting process has been the long set-up time required by cast articles in the mold. This has meant that a large quantity of molds was required to achieve commercial production rates, resulting in the use of large amounts of floor space and labor [5].

Recent technical developments have resulted in pressure casting, an alternative forming process, which offers the intricate shape capabilities of slip casting while approaching the faster production rates of pressing and plaster forming [5].

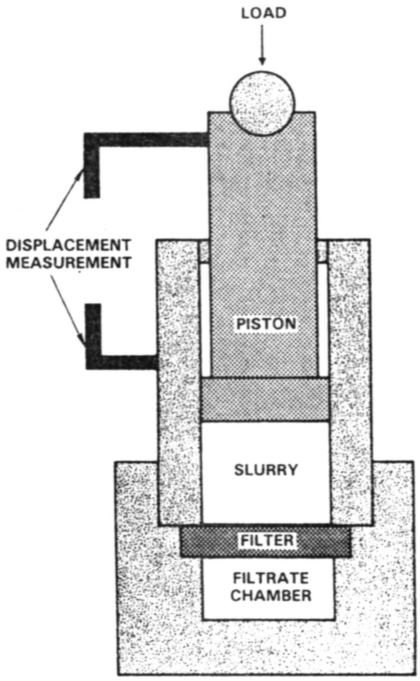

Figure 5.6. Schematic diagram of the pressure-filtration device [61]

5.2.1. Pressure Filtration

The main difference between traditional casting and pressure casting is that the cast formation in the pressure-casting process is not based on the principle of pressure filtration. Therefore, the basic concept of pressure casting is not entirely new. As early as 1917, there was a patent application dealing with this process. In fact, the ceramics industry has used this principle for many years in the form of the filter press. The pressure-casting process is directly comparable to filter pressing, with the basic difference being that the filter medium in the pressure-casting machine must both filter and shape the end product [5].

Because the pressure-casting operation is basically a filtering operation, established filtration equations, in a somewhat simplified form, are applicable. The following is the equation for body thickness on a filter [5]:

$$D_s = \sqrt{\frac{P.t}{W_s} + \left(\frac{W_f.D_f}{W_s}\right)^2} - \frac{W_f.D_f}{W_s} \tag{5.7}$$

where D_s denotes thickness of the body. Here, P, t and W_s represent filtration pressure, time and resistance of body, respectively. W_f and D_f stand for filter resistance and thickness.

Because of the very high porosity of the special mold materials developed by Netzsch [5], we have found that the two factors relating to filter resistance (W_f) are negligible. Therefore, the thickness of the body becomes a function of the filtration pressure, filtration time, and filtration resistance of the body. The equation then simplifies to:

$$D_s \approx \sqrt{\frac{P.t}{W_s}} \tag{5.8}$$

Body thickness is directly related to the slip pressure at any given casting time. As the slip pressure increases, however, the hydraulic pressure on the mold also increases. The materials of construction and the tolerances of fit become increasingly critical and more expensive to achieve as the slip pressure increases [5].

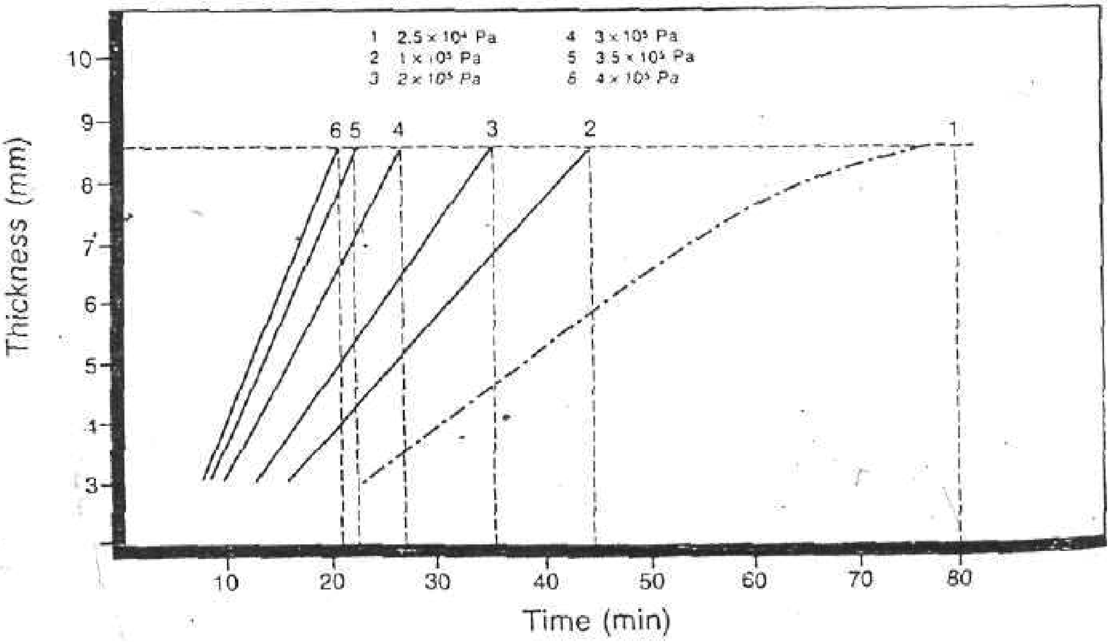

Figure 5.7. The thickness formation is compared between traditional battery casting and casting with overpressure application [5]

This leads to the conclusion that different manufacturing systems are required for different applications. By using a medium level of pressure (3.5-4.0 bar) on large, high-production pieces, such as sanitaryware, improved productivity can be achieved at lower capital cost. Figure 5.7 shows the rapid improvement in casting time as the slip pressure is increased from 0.25-4.0 bar (Figure 5.7). The time required to build a body thickness of 8.5 mm is reduced from 80 min to 21 min. Increasing the pressure above 4.0 bar will, obviously, continue to shorten the set-up time, but at a continually decreasing rate and at a continually escalating cost in terms of mold material and equipment requirements [5].

5.2.2. Higher Pressure for Production of Smaller Shapes

On smaller, more complex shapes and lower production levels, higher pressure casting becomes more advantageous. The faster dewatering time achieved at the higher slip pressure, together with relatively faster demolding procedures, decreases floor space requirements. Faster mold change-over time leads to better production conditions. Experience has shown that slip pressures up to 40 bar are successful and economically reasonable [5].

Figure 5.8 shows a gain of time of more than 20 sec with a pressure increase from 20-30 bar on a wall thickness of 6 mm. An increase from 30-40 bar reduces the time by another 15 sec, while a further increase to 50 bar brings a gain of only 10 more sec. A greater decrease in forming time without additional machine construction expenditure can be achieved, however, by trying to reduce the filter resistance of the body, which means component modification to the slip. This can mean a change in the water content as well as a modification of the body composition [5].

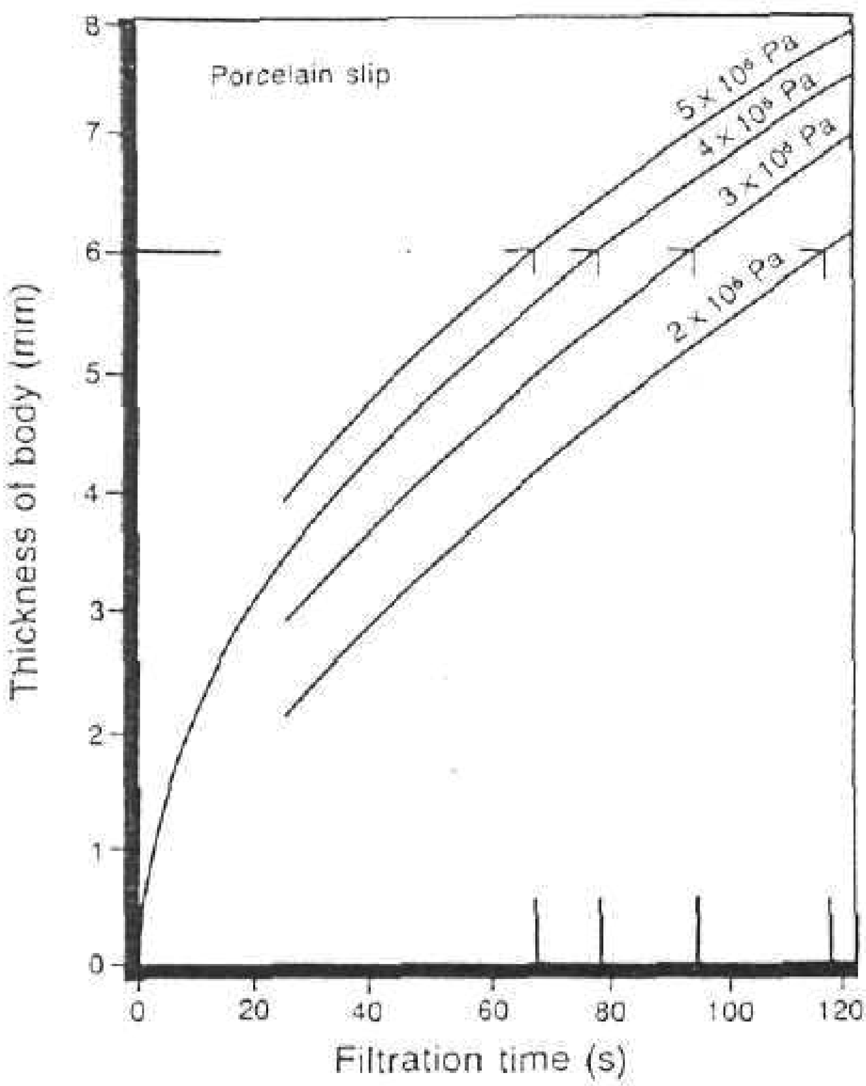

Figure 5.8. The growth of a body during pressure casting is a function of the filtration pressure [5]

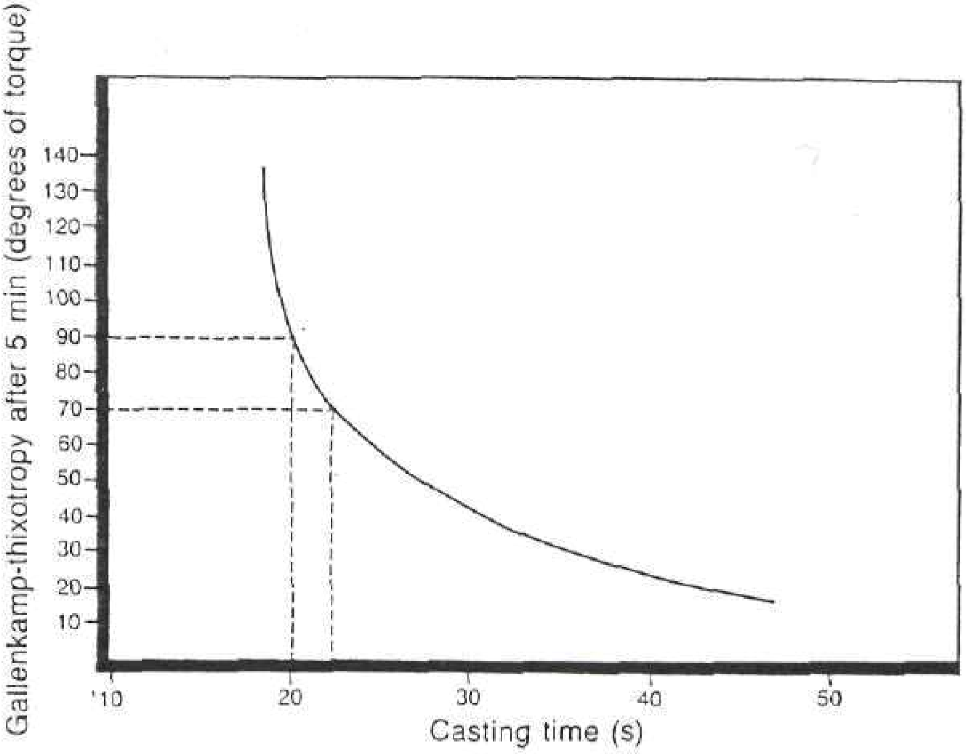

Figure 5.9. The casting time (thickness formation time for 8.5 mm) is a function of the thixotropy of the slip [5]

Figure 5.9 shows the effect of the thixotropy of the slip on formation time. By decreasing the slip thixotropy, the filtration resistance factor is reduced and a decrease in formation time follows. Figure 5.10 shows the differences for various ceramic bodies in a high-pressure casting system. With a cast thickness of 6 mm, formation times of approximately 65 sec are achieved with a porcelain body, while approximately 240 sec is required for an earthenware body [5].

With the high-pressure casting system, slip pressures up to 40 bar are practical. It is evident that for such slip pressures, plaster would be unsuitable as a material for the molds. Only a small fraction of this pressure would cause the molds to break, which is why Netzsch developed a plastic material that combines high porosity, high-mechanical strength, and good elasticity. This material is able to successfully operate in high-pressure casting conditions [5].

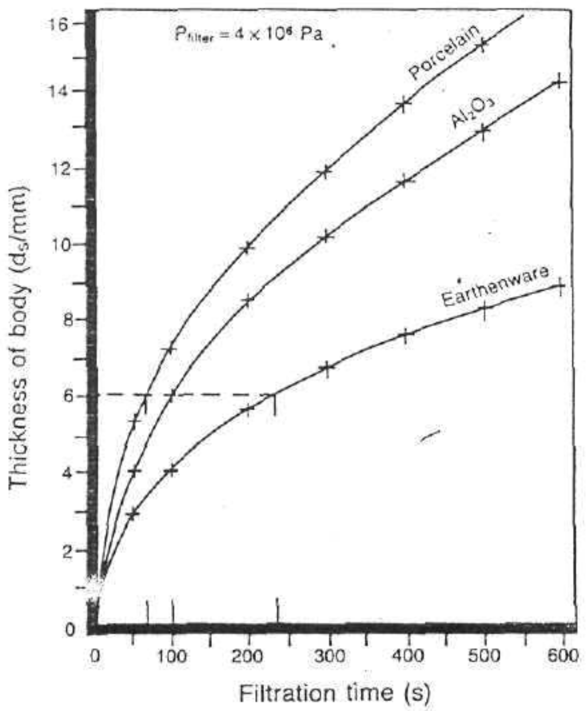

Figure 5.10. The growth of the body (thickness) depends on the type of batch material [5]

The necessity of porosity and strength in a pressure-casting mold is evident, but why elasticity? The amount of flash on the finished piece, as well as the maximum possible article size, is in the hands of the mold maker. The better the two mold halves fit, the less finishing will be required after casting. The flatter the two sealing surfaces between mold halves, the lower the closing force that is required. Conversely, the maximum possible article surface area will be larger if the mold maker can produce flatter and truer sealing surfaces [5].

Since the mold maker can never achieve perfect flatness, a degree of elasticity is needed in the mold material so that the small remaining differences or deviations from parallel can be equalized by the fit under the closing pressure [5].

5.2.3. Design Requirements of Pressure Slip Cast Equipments

A typical high-pressure casting machine is mounted on a structure which accommodates the complete equipment supply, i.e., vacuum, compressed air, water with the appropriate regulating and distribution elements, the switchboard, and the closing device. A separate hydraulic unit is either coupled to the machine structure or can be placed separately nearby. It serves for both the actuation of the closing device and the formation of the slip pressure. A self-aspirating, hydraulically actuated diaphragm pump supplies the slip into the die, which is located between head plate and slide plate [5].

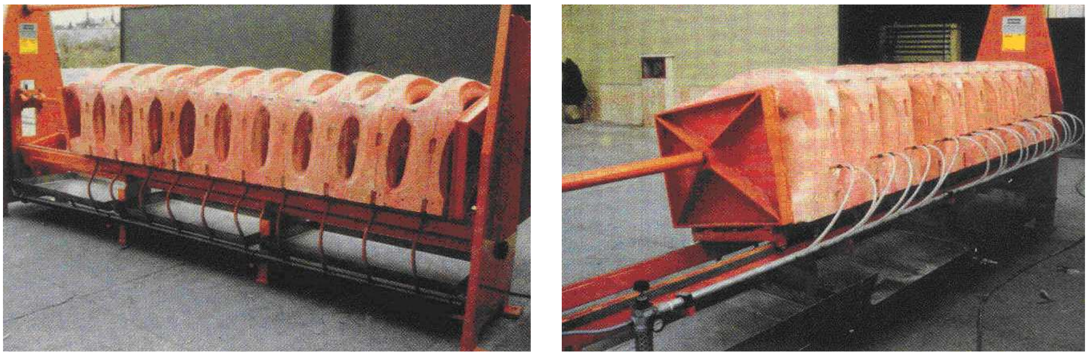

Figure 5.11. A medium pressure casting machine can come with a series of plastic molds mounted on a bench-type frame and hoses that provide air for dewatering the molds [5]

When working in a typical configuration, the article is removed by means of a vacuum pickup. After fettling the article at the filling point and smoothing any casting seam with a sponge, the article is set aside for drying [5].

There are, however, articles or situations when it is useful to work with a horizontal die instead of a vertical one. For this purpose, the machine is equipped with a hydraulic pivoting device. This allows the molds to be placed in the most desirable position for both production and testing purposes [5].

Milled, T-shaped notches in the supporting plates help to fix the two halves of the die so that, in connection with the centering locks, the two halves of the die can be changed quickly and easily. The dies can be designed either as single-cavity dies, or, for smaller articles, also as multi-cavity dies [5].

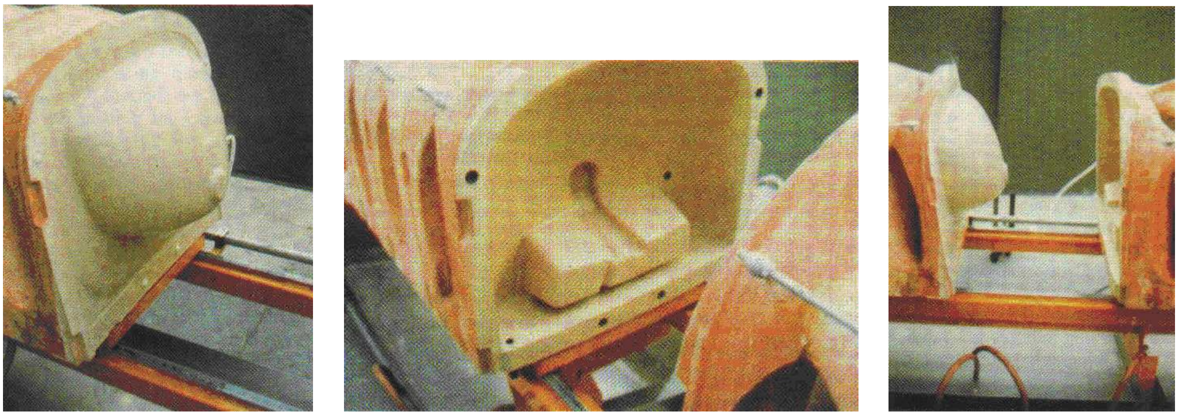

Figure 5.12. Views of molds in medium pressure casting machine [5]

The machine is operating with an adjustable maximum closing force of 65 tons. The maximum possible article surface is approximately 1000-1200 cm^2. It is, as already mentioned, partially limited by the parallelity of the two die halves. Machine design also limits the overall mold area to 500 mm × 600 mm size [5].

The machine is suitable for the production of different articles in various ranges from a simple chinaware dish from porcelain up to a complicated part from a fine-ground special technical ceramic [5].

5.2.4. Medium Pressure for Increased Production Rate

When larger parts and higher production levels are required, the medium-pressure casting system is used. This system utilizes either a series of special plaster-based molds or a series of plastic molds mounted on a bench-type frame. When casting, slip is pumped into each mold simultaneously and pressurized to between 3 and 4 bar [5].

After the casting process is completed, the parts are demolded individually and set aside for final drying. The molds are dewatered via an air-purging process. The molds are then ready for immediate use. The entire production cycle takes approximately 75 min with a 15-mold bench [5].

Both the high- and medium-pressure casting system utilize molds with a very long life compared to the standard plaster molds currently used. As it is well known, the production of standard plaster molds is costly to use because they will wear out rapidly, they must be dried frequently, they can cause fluctuations in quality owing to varying moisture contents within the mold and degrees of fit between mold parts, and they require a large storage area when not in use [5].

All these inconveniences are reduced or eliminated by the use of pressure-casting production techniques. Since mold drying is not necessary, the manufacturer is free to choose the location of the pressure-casting machine within the plant. The expenditure of time and work for changing from one model to another is significantly reduced. Little storage area is required for molds for shapes not currently under production [5].

Pressure casting results in a more efficient dewatering of the article. The lower moisture content of the cast part minimizes the risk of deformation when being taken out of the mold. In addition, this means shorter drying times and less susceptibility to stresses, which leads to deformations during drying or to cracking [5].

The quality of the parts is considerably improved as well. Erosion of the surface of the molds is virtually eliminated. The pressure-cast parts have a much smoother surface and, above all, a consistently smooth surface. Embossments, edges, and borders remain constant, which means that the last cast from a mold will be as good as the first one. Variable body thicknesses can be shaped far better than with traditional casting. The cast compression of the pressure-cast article is higher than with a normally cast one. This results in lower shrinkage during drying and firing, and thus, better accuracy of the finished piece, as well as higher mechanical stability of the fired body [5].

Working conditions are considerably improved with pressure-casting systems. Thanks to the higher stability of the cast part, it is possible to finish the part during demolding instead of fettling the white-dried ware. Fettling the casting seam with the help of a sponge is the only requirement. This can usually be done by the person operating the machine. In practice, this can mean the saving of fettling personnel. Since the machines do not require mold drying, they can be installed outside of the warm and moist atmosphere of a typical casting department. In addition, quality of production is no longer dependent on the abilities of the caster; quality is now determined by the machine and the mold [5].

5.2.5. Reduction in Operating Cost with Pressure Slip Casting

Optimum machine efficiency is obtained if one person operates two or three machines simultaneously on a two- or three-shift operation. With this type of operation, a considerable reduction of personnel costs and amortization time is achieved. The possibility of economic production of short-run articles, together with the short time necessary to execute orders, allows for fast response to changing market situations [5].

As with almost any production equipment, the most important factor is the effect on worker productivity and production costs. Pressure casting improved both at various factories around the world. At a large sanitary ware factory in northern Italy, three medium-pressure casting benches had been in operation for some years. Two benches had handled vitreous China while the third had produced fireclay articles. The casting cycle had been reduced to approximately 55 min using a heated slip. One operator and a part-time assistant had handled the production of all three of the 15-mold benches on each shift [5].

The casting benches had operated steadily on a two-shift-per-day basis. No drying was required for the specially constructed molds, either between casts or during an idle shift. For this reason, three shifts of production per day had been possible. Casting costs had been reduced by approximately 16 % to 18 %, compared to traditional casting methods [5].

The production of 34-cm oval platters had been performed on two high-pressure casting machines at a German porcelain dinnerware company. One operator per shift had casted and fettled between 550 and 600 platters. The reduced finishing requirements and the high accuracy of the cast piece almost had eliminated casting losses [5].

The cast quality of the ware had remained uniformly high from operator to operator because of the automatic control features of the machine. As a result, the production cost of each pressure cast piece was about 0.55 less than that of a conventionally cast piece, including the amortization cost of the equipment. Obviously, pressure casting can offer a faster, more economical method to produce high-quality, precision cast pieces of all shapes and sizes [5].

6. EXPERIMENTAL STUDY

Slip casting is an attractive forming method and is used widely in the commercial production of ceramics. One of the most favorable characteristics for the method is the high quality of products, which is often ascribed to their good microstructures realized with this particular processing [50].

Pressure slip casting is a further development of the conventional slip-casting technique where polymeric moulds are used instead of plaster moulds and the application of high pressure gives a more efficient and reliable manufacture of ceramic components. Pressure slip casting is nowadays an established forming technique in the fabrication of traditional clay-based ceramics (pottery and sanitary ware). Commercial production of engineering ceramics is still very limited [51].

Slip rheology is very important in casting process. Slip rheology is directly affected with particle surface chemistry that regulates repulsion and attraction forces between particles. The control of surface chemistry while preparing low-viscosity suspension that are highly concentrated with powders is a major requirement of slip casting. Low viscosities are needed for pourability, and high solids concentrations (up to 60 vol % solids) are needed to maximize the casting rate and "green" density. Traditional methods for achieving low-viscosity concentrated suspensions entail the use of polydisperse particle size systems and repulsive interparticle forces that arise from surface-adsorbed ions or polymers [52].

A key factor is related to the packing density and packing homogeneity of the green body. For traditional ceramics, the achievement of the high packing density is generally required to reduce the shrinkage during the firing stage. Commonly the powder consists of graded particle size fractions. Geometrical particle packing concepts provide a useful basis for understanding how the structure of the green body develops. For advanced ceramics, both the packing density and the packing homogeneity are important. The powder characteristics and the forming method control the particle packing of the green body which, in turn, has a significant influence on the micro structural development during sintering. Large variations in the packing density lead to the development of micro structural heterogeneities (such as large voids) during the sintering step, thereby limiting the ability to achieve high density and fine grain size [53, 54].

Additives are widely used to aid the forming operation as well as to control the microstructure of the green body. In the forming process, they serve a variety of functions dispersants (also referred to as deflocculants). Dispersants are either inorganic or organic substances. They act to stabilize a suspension against flocculation and so play a key role in the casting methods (slip casting and tape casting) [53, 54].

Ceramic powders have tendency to agglomerate due to the attractive intra-particle Van der Waals forces. This tendency can be eliminated with the addition of appropriate dispersants which alter the powder surface properties so that repulsive forces, either due to electrostatic repulsion resulting from overlapping of electrical double layers or due to steric hindrance resulting from absorption of large molecules, become higher than the attractive ones and the particles can remain separated in suspension [57]. Dispersant addition can dramatically reduce the viscosity of slurries with very high solids content, thus ceramic industry has a constant demand for effective dispersants or deflocculants [58, 59].

The common deflocculants used in water are separated as inorganic and organic deflocculants. Common inorganic deflocculants are Sodium carbonate, Sodium silicate, Sodium borate and Tetrasodium pyrophosphate. Common organic deflocculants are Sodium polymethacrylate, Ammonium polyacrylate, Sodium citrate, Sodium succinate, Sodium tartrate, Sodium polysulfonate and Ammonium citrate.

For the same powder, different forming methods can lead to significant differences in the packing homogeneity in the green body. When compared to dry or semi-dry pressing (e.g., die pressing), slurry-based methods (e.g., slip casting) can lead to improved packing homogeneity. The influence of packing homogeneity on sintering has been well documented in the ceramic literature. For the same green density, improved packing homogeneity leads to improved sinterability in the form of higher sintered density at a given sintering temperature and the ability to achieve high density with fine particle size [53, 54].

The advantages of pressure slip casting method are not only economically convincing [60]. General advantages are;

- Molds can be changed in a very short time.
- Even after a long period of operation the molds do not show any wear which is common to plaster of paris.
- With adequate intermediate storage, the molds can be re-used as reused as often required. Acceptable number of casts, as with plaster (age of plaster molds), need not to be considered.
- Minimal storage space is needed.
- No more handling of plaster molds (transport, removal, etc.) is necessary.
- The capacity for the production of plaster molds can be reduced.
- Fettling, i.e. removing minimal seems and cutting out certain parts is possible immediately after taking out the casts. Fettling of the dry ware is no longer necessary.
- More human working conditions prevail, due to normal room temperatures, elimination of dust, and draughts caused by fans.
- Physical strains can be avoided with mechanic or automatic devices for taking out the casts, the caster becoming a machine operator.
- Training takes only a few days to a few weeks.
- Return of slip for hollow cast is no longer necessary as the return immediately processed (it is no longer necessary to collect and re-prepare the slip)
- Far less space than for battery casting or conventional unit is needed.
- Energy consumption is reduced to a minimum.
- Two or three shift operation possible at once without additional costs (impossible with plaster molds).
- The workers have less influence on the quality of the product since they no longer

prepare the plaster molds; casts are removed mechanically or automatically and less labor is required for fettling.

6.1. Materials Used in Experiments

The starting material was commercially available α-Al_2O_3 (Aluminium Pechiney, France) with a mean diameter $\sim 1\ \mu$ m. Alumina is the most widely used oxide ceramic material. Alumina have important characteristics of high compression strength, hardness, thermal conductivity, refractoriness, dielectric strength, electrical resistivity and resistant to abrasion, thermal shock and also chemicals. The major uses of Alumina are pump seals, electronic substrates, grinding media, abrasion resistant tiles, cutting tools, bioceramics, (hip-joints), body armour, laboratory ware and wear parts for the textile and paper industries.

Sodium silicate was used as a deflocculant and Natrium alginate was used as binder. Sodium silicate (Na_2SiO_3), the most popular deflocculant, which is effective, reliable and inexpensive, is used in casting slips for many years.

A list of materials and the slip composition (wt %) used in the experiment are given in Table 6.1, Table 6.2 and Table 6.3.

Table 6.1. Materials used in preparing ceramic slips

Ingredients	Material
1	α-aluminium oxide ($\sim 1\mu m$ and % 99 pure)
2	Yttrium oxide or Nickel oxide and Magnesium oxide
3	Natrium alginate
4	Sodium silicate
5	Distilled water

Table 6.2. Slip Composition (Slip 1, Slip 2, Slip 3), wt %

Ingredients	Material	Slip Composition (wt %)
1	α-aluminium oxide ($\sim 1 \mu m$ and % 99 pure)	65.15
2	Yttrium oxide	0.1
3	Natrium alginate	0.026
4	Sodium silicate	0.886
5	Distilled water	33.83

Table 6.3. Slip Composition (Slip 4), wt %

Ingredients	Material	Slip Composition (wt %)
1	α-aluminium oxide ($\sim 1 \mu m$ and % 99 pure)	65.15
2	Nickel oxide (%50), Magnesium oxide (%50)	0.16
3	Natrium alginate	0.026
4	Sodium silicate	0.886
5	Distilled water	33.77

6.2. Equipment Manufactured and Used in Experiments

In the production of a ceramic green body, a conformable mold design plays an important role to achieve the manufacturing process successfully. Throughout the laboratory testing period, several set-ups were utilized. Slip casting experiments were done with plaster of paris mold. Pressure slip casting experiments were done with specially designed pressure casting set-up. For this purpose, two pressure casting set-ups have been designed. First one was mainly designed as an aluminium case and a stainless steel pressure chamber. The second one was designed as Polyethylene case and steel support.

Aluminium and stainless steel pressure slip casting experiment set-up consisted of four main parts. These are listed below;

a) Aluminium bottom case
b) Stainless steel cylindrical pressure chamber (80 mm inner diameter)

c) Piston

d) Steel cap for bedding of piston

The aluminium bottom case contains the mold which provides the expulsion of water. The prepared alumina slip was poured from top of the steel cylinder onto the mold. The pressure slip casting set-up was adapted to a hydraulic press. The detailed technical drawings of the pressure slip casting set-up are given in the Appendix A.

Figure 6.1. Aluminium pressure slip casting set-up

The Polyethylene pressure slip casting experiment set-up consisted of three main parts. These are listed below;

a) Polyethylene bottom case

b) Polyethylene piston

c) Steel support

The polyethylene bottom case contains the mold which provides the expulsion of water. The alumina slip prepared was poured onto the mold that was placed in the bottom case. The pressure slip casting set-up was adapted to a hydraulic press. Pressure was applied by the piston of the set-up.

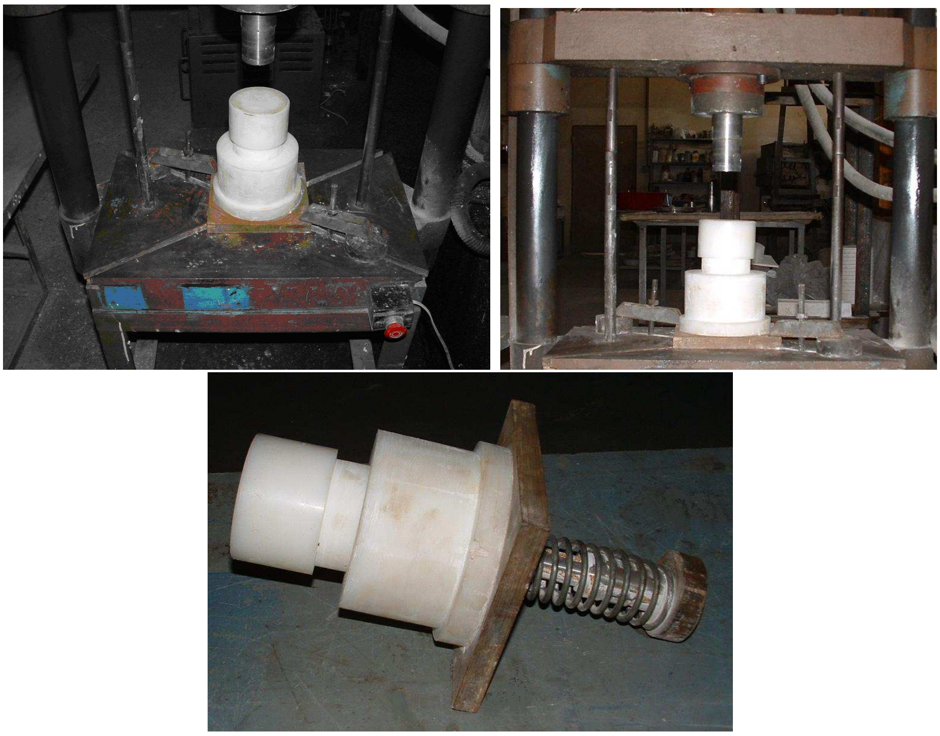

Figure 6.2. The polyethylene pressure slip casting set-up

6.3. Production of a Slip Casting Mold

A mixture of about 40 wt % water and 60 wt % plaster of paris was prepared using about 1000 gr water to 1500 gr plaster of paris. The mixture was soaked for 3 minutes and then mixed for 4 minutes. It was casted into a wooden chamber and dried. Finally, the plaster of paris mold was taken outside. When it was dried, it was given required dimensions (80 mm in diameter and 30 mm in depths) to use for slip casting purpose.

Figure 6.3. Plaster of paris molds

6.4. Production of a Pressure Slip Casting Mold

Pressure slip casting molds are special molds which are very expensive. Here, this problem was solved by producing a special ceramic mold. The procedure for manufacturing the ceramic mold was as follows. The water component was poured slowly onto the aluminium oxide and bentonite [(Na, Ca) (Al, Mg) 6(Si_4O_{10}) 3(OH) 6.n H_2O] powder mixture. When bentonite clay absorbs water and swells, it is stretched open like a highly porous sponge. During this process, the aluminium oxide and bentonite powder mixture were mixed with water. Then, this green was put into a plaster of paris mold to give a cylindrical form, appropriate with final pressure slip cast alumina ceramic part. When the green was formed, it was sintered for about 12 hours. At this time period, when the furnace temperature reached to (1350 °C), it was fixed at this temperature (1350 °C) for 4 hours. After this process, these produced ceramic molds were cooled down to room temperature and the shape with the desired dimensions (80 mm, diameter) was achieved for the purpose of usage as pressure slip casting mold.

Table 6.4. The composition of the pressure slip casting mold body, wt %

Ingredients	Material	Composition(wt %)
1	α-aluminium oxide ($\sim$ 1 μm)	80
2	Bentonite	8
3	Distilled water	12

Figure 6.4. The ceramic pressure slip casting molds, shaped in plaster of paris mold

6.5. Slip and Pressure Slip Casting of Alumina

The casting procedure involved the slip and pressure slip casting of Al_2O_3 into cylindrical shapes. As techniques, slip casting and pressure slip casting processing were utilized. These processes consisted of four main steps as mentioned below:

1. Slip preparation
2. The slip and pressure slip casting process
3. Drying
4. Sintering

All of these steps have been investigated and then cylindrical alumina ceramic compact parts were produced.

For slip preparation, the dispersant was essential. It helped to prevent the reagglomeration of the particles after they have been broken down during the milling operation and served to reduce the viscosity during this step. It permitted the use of a higher particle concentration in the slip casting slurry which was beneficial for improving the packing density in the dried cast and for reducing cracking during the drying step [53, 54]. In this study, sodium silicate was used as dispersant.

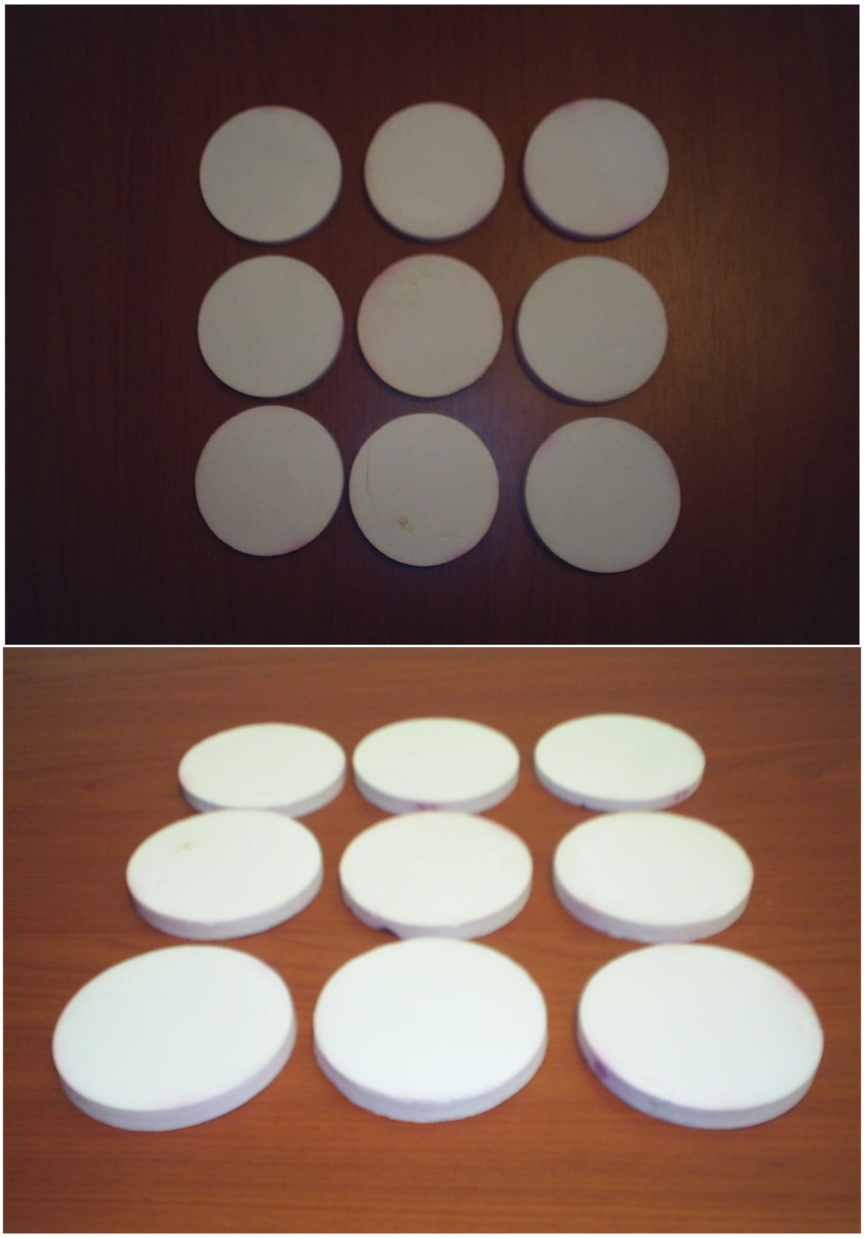

Figure 6.5. The produced cylindrical alumina ceramic compact parts

In the dispersion milling step, the ceramic powder, the binder and the dispersant were introduced into the ball mill. The ceramic jar was commonly a half filled with alumina slurry and the remainder of the ceramic jar was filled with the alumina balls to about % 75 of the mill volume. Purpose of this step was particle size homogenization and to break up the powder agglomerates and to coat each particle with a layer of the dispersant.

Distilled water, sodium silicate, to increase the wettability of the powders and ammonia, to adjust the pH values of the suspension and natrium alginate, to improve green body strength were added to the slurry. Finally, Al_2O_3 and Y_2O_3 powders were added to ball milling tank. Al_2O_3 slurry was homogenized with ball milling. The powder content was 66 wt % in the slip. Detail of the ingredients for the slurry is given in Table 6.2. For ball milling, mixed size of Al_2O_3 balls were used. PH values were adjusted between 9 and 10 by ammonia and hydrochloric acid during ball milling. Then, the slurry in the tank was circulated and ball milled. Ball milling was done for different time periods (about 24, 36, 45 and 56 hours) to observe the effect of milling time. After this period, the slurry was circulated again for 1 hour at a slower speed to remove the entrapped air.

For the slip casting experiments, plaster of paris molds were used to form alumina ceramic compact parts. For this purpose, the plaster of paris mold was filled with the required amount of slip to produce samples that are 80 mm in diameter and 10-20 mm in height. Small amount of slip was added from time to time to maintain a fairly flat surface. When the liquid was extracted from the mold walls (It was taken nearly 10 minutes), the casting was removed after partial drying. Then, the castings were dried for 24 hours at 100 °C in a furnace. Finally, sintering was carried out with reaching to different temperatures 1175, 1250, 1300, 1570, 1600 and 1650 °C to observe sintering temperature effect on castings.

For the pressure slip casting experiments, after preparation of slip, pressure slip casting set-up was adapted to a hydraulic press and ceramic mold was placed to the bottom case of the set-up. Because of high pressure on the slip, the green product was sticking on the ceramic mold's surface. In order to prevent this problem, filter paper was put on the upper surface of the ceramic mold to make easy removal of the casting from the mold. After pouring the slip onto the ceramic mold, 2 MPa pressure was applied by hydraulic press with piston. Later on, cylindrical alumina compact parts were produced (It was taken nearly 30 seconds), and removed from the set-up carefully. In order to remove water from the green product without having any defect, the alumina parts were dried for 24 hours at 100 °C in a furnace. Finally, sintering was carried out with reaching to different temperatures 1175, 1250, 1300, 1570, 1600 and 1650 °C to observe sintering temperature effect on castings.

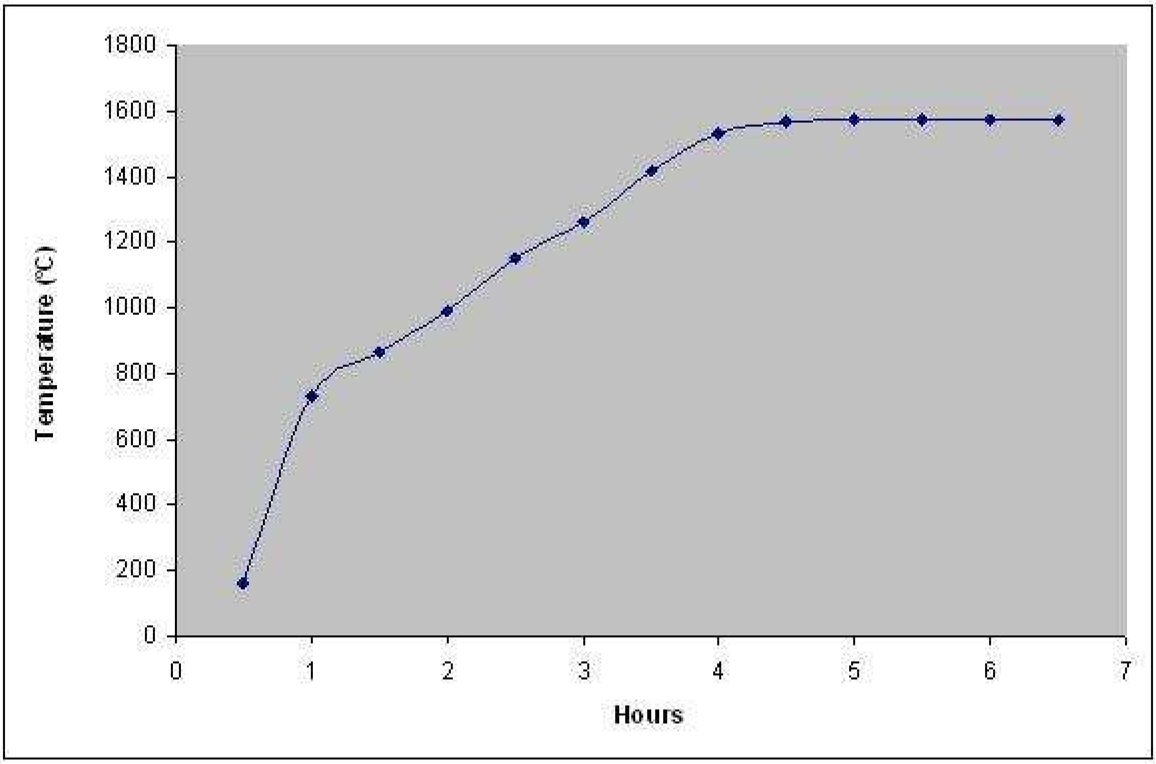

Figure 6.6. The variation of furnace temperature in sintering of Alumina at 1600 °C

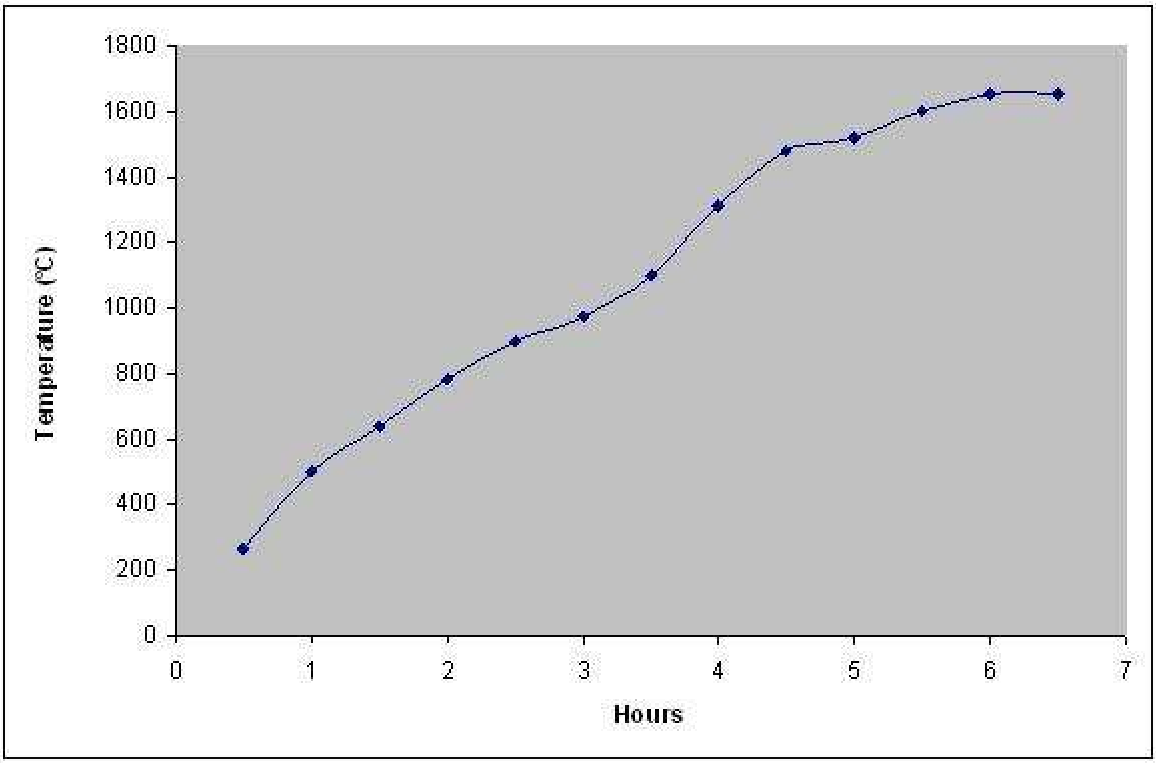

Figure 6.7. The variation of furnace temperature in sintering of Alumina at 1650 °C

7. RESULTS AND DISCUSSION

7.1. Porosity and Shrinkage of Specimens

For porosity test, the sintered specimens were weighted and then these specimens were boiled in water. These samples that absorbed water were weighted again to determine difference in weight. The percentage of porosity was found with the following formula:

$$W = \frac{W_2 - W_1}{W_1} \times 100 \tag{7.1}$$

where W, W_1, and W_2 denote water absorption, dry weight and final weight after water absorption, respectively.

For shrinkage test, the sintered specimens were measured to determine the decrease in diameter. The percentage of shrinkage values of the specimens were found with the following formula:

$$S = \frac{S_1 - S_2}{S_1} \times 100 \tag{7.2}$$

where S, S_1 and S_2 designate shrinkage value of specimen, initial diameter of specimen and final diameter of sintered specimen, respectively.

Table 7.1. and Table 7.2. shows the percentage of porosity and shrinkage values for the slip and pressure slip cast specimens after sintering.

Table 7.1. Percentage of porosity and shrinkage of slip cast specimens

Slip Cast Specimens				
Slip Type	Milling Period (Hours)	Sintering Temperature (° C)	Porosity (%)	Shrinkage (%)
Slip 2	36	1175	22.24	0.85
		1600	9.05	10.41
		1650	5.83	12.81
Slip 3	45	1300	19.40	1.85
		1600	8.91	9.51
Slip 4	56	1250	17.42	3.98
		1600	5.12	13.40

Table 7.2. Percentage of porosity and shrinkage of pressure slip cast specimens

Pressure Slip Cast Specimens				
Slip Type	Milling Period (Hours)	Sintering Temperature (° C)	Porosity (%)	Shrinkage (%)
Slip 1	24	1175	22.11	0.86
		1600	9.12	10.47
Slip 2	36	1175	21.82	0.75
		1570	9.16	9.68
		1600	8.60	10.24
		1650	5.70	12.58
Slip 3	45	1570	9.06	8.08
		1600	8.02	9.14
Slip 4	56	1250	16.25	3.75
		1600	5.05	13.24

At the beginning, The fine and coarse powder combined in the slurry with a solid content of % 66 was used since it corresponds to the solid loading that promoted the highest packing density.

The distribution of particle sizes in a processing system has a significant effect on the particle packing and pore structure and the behavior during forming, drying, and firing. The packing density increases, when the particle size and porosity decrease and solid loading increases.

In slip casting method, particles' segregation can be a problem. This phenomenon causes inhomogeneous microstructures and low mechanical resistance. The gravity force and particle size ratio are the main causes of particle segregation. Milling time makes the particle size distribution narrower in the slip. Increase in milling time causes to decrease in viscosity of the suspension (deagglomeration/milling effect). These results the less resistance to flow and means improved particle packing ability. The cast compression of the pressure-cast article is higher than with a slip cast one. This results in lower shrinkage during drying and firing, and better accuracy of the finished piece, as well as higher mechanical stability of the sintered body.

Experiments showed that increasing temperature in sintering process gave the better results. The percentage of shrinkage value increased and the percentage of porosity value decreased with increasing temperature in sintering process. On the other hand, using nickel oxide, and magnesium oxide as sintering aids in Slip 4 gave better porosity and shrinkage values, when compared using yttrium oxide as sintering aid in Slip 1, 2, and 3. For example, In 1600 °C, Slip 4 had % 5.05 of porosity and % 13.24 of shrinkage. At the same sintering temperature, Slip 1, 2, and 3 had % 9.12, % 8,60, % 8.02 of porosity and % 10.47, % 10.24, % 9.14 of shrinkage. The results showed that nickel oxide and magnesium oxide are more effective sintering aids for alumina, when compared with yttrium oxide.

From the experiments, the mean density of sintered slip cast alumina compact parts for Slip 1, 2 and 3 was found 2.8 gr/cm^3 (3.14 gr/cm^3 for Slip 4), and the mean density of sintered pressure slip cast alumina compact parts for Slip 1, 2 and 3 was found 2.9 gr/cm^3 (3.22 gr/cm^3 for Slip 4) at 1600 °C. In addition, the mean density of sintered slip cast alumina compact parts for Slip 2 was found 3.12 gr/cm^3 and the mean density of sintered pressure slip cast alumina compact parts for Slip 2 was found 3.21 gr/cm^3 at 1650 °C. Finally, produced alumina compact parts should be sintered above 1600 °C. Because, this temperature did not sufficient to reach theoretical density.

7.2. Three Point Bending Test and the Weibull Analysis of the Fractured Test Specimens

Three point bending tests were done at Tübitak MAM-Gebze. The tests were done at room temperature using a Zwick 250 Universal Test Machine. Distances between supports were taken as 40 mm.

The specimens were dimensioned to be 4 × 10 × 50 mm for the three point bending test. Table 7.3-7.6 shows the three point bending test results for both slip cast specimens and pressure slip cast specimens.

Ceramic compact parts, produced by identical methods fail at very different applied loads. This is a characteristic of ceramic materials which are naturally brittle and also very sensitive to defects, notches, etc.

In order to design ceramic parts, the probability that a flaw is present that will cause failure to occur at any given stress must be known. The Weibull distribution and Weibull modulus provide one statistical approach in designing with ceramics [55].

The probability of failure (P) can be related to the failure stress by;

$$\ln\left[\ln\frac{1}{(1-P)}\right] = m\ln f \tag{7.3}$$

where P is the cumulative probability of failure, f is the stress at which failure occurs, and m is the Weibull modulus. When the applied stress is high, there is a high probability that any sample will fail. As the stress decreases, the probability that any sample will fail also decreases. Even for low applied stresses, there is a finite possibility that a sample contains a flaw large enough to propagate. It is a small probability, even at low stresses, that limits the use of ceramic materials for critical applications [55].

The Weibull modulus m is the slope of the cumulative probability curve. For design of critical, load bearing ceramic parts, the Weibull modulus should be large; a high slope represents a ceramic with a narrow range of flaw sizes and helps us design more reliable parts [55].

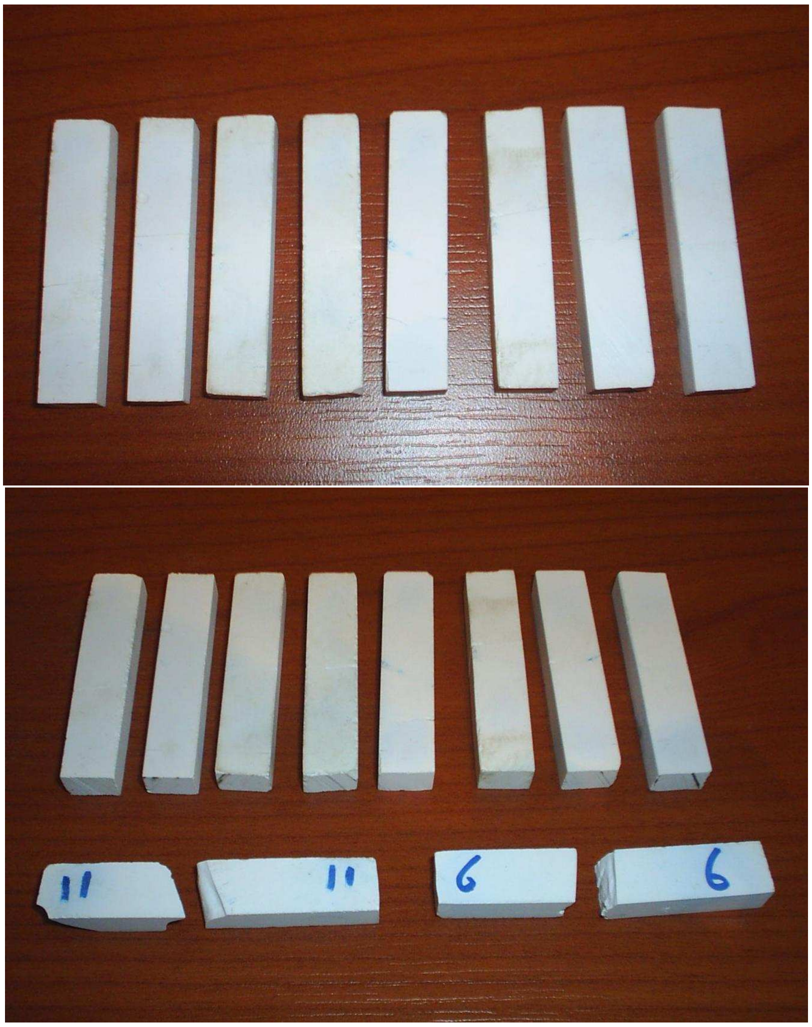

Figure 7.1. Three point bending test specimens (4 × 10 × 50 mm)

Table 7.3. Three point bending test fracture strengths (Kg_f/mm^2) of the slip cast specimens

Slip Cast Specimens
Three Point Bending Fracture Strength (Kg_f/mm^2)
14.47
13.62
15.70
9.97

Table 7.4. Three point bending test fracture strengths (Kg_f/mm^2) of the pressure slip cast specimens

Pressure Slip Cast Specimens
Three Point Bending Fracture Strength (Kg_f/mm^2)
13.71
9.45
8.99
12.50
12.05
12.76
13.63
9.07
12.78
10.69
12.37

A) For our slip cast specimens, The total number of specimens n = 4 The cumulative probability P is then the numerical rank divided by n+1=5. We can then plot $\ln[\ln(1/(1-P)]$ versus $\ln(\sigma_f)$. The following Table 7.5 and Figure 7.2 show the results of these calculations for slip cast specimens.

Table 7.5. Weibull analysis of the slip cast specimens

ith specimen	σ_f (Kg_f/mm_2)	P	ln[ln (1/(1-P)]
1	9.97	1/5=0.2	-1.499
2	13.62	2/5=0.4	-0.672
3	14.47	3/5=0.6	-0.087
4	15.70	4/5=0.8	0.476

The slope of the best fitting line in Figure 7.2 is the Weibull modulus m;

$$m = \frac{(0.5)-(-1.5)}{\ln(16)-\ln(10)} = 4.26 \tag{7.4}$$

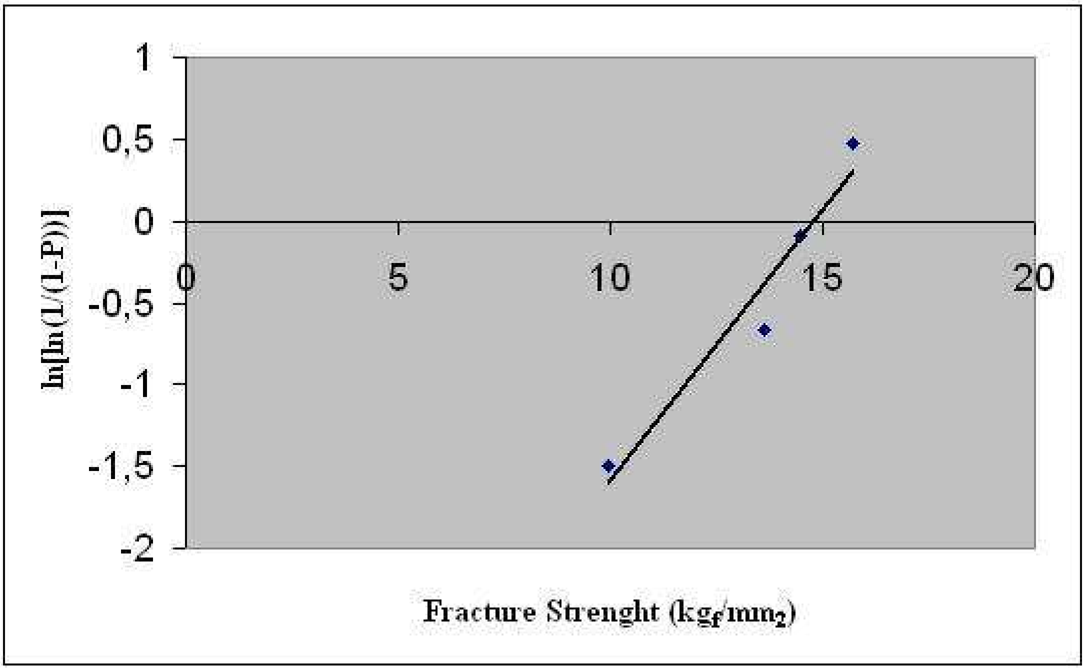

Figure 7.2. Fracture strength of the slip cast specimens

B) For our pressure slip cast specimens, The total number of specimens $n = 11$ The cumulative probability P is then the numerical rank divided by $n + 1 = 12$. We can than plot $ln[ln(1/(1 - P)]$ versus $ln(\sigma f)$. The following Table 7.6 and Figure 7.3 show the results of these calculations for pressure slip cast specimens.

Table 7.6. Weibull analysis of the pressure slip cast samples

ith specimen	σ_f (Kg_f/mm_2)	P	ln[ln (1/(1-P)]
1	8.99	1/12=0,083	-2,446
2	9.07	2/12=0,167	-1,699
3	9,45	3/12=0,250	-1,246
4	10,69	4/12=0,333	-0,903
5	12,05	5/12=0,417	-0,617
6	12,37	6/12=0,500	-0,367
7	12,50	7/12=0,583	-0,134
8	12,76	8/12=0,667	0,095
9	12,78	9/12=0,750	0,327
10	13,63	10/12=0,833	0,582
11	13,71	11/12=0,917	0,912

The slope of the best fitting line in Figure 7.3 is the Weibull modulus m, is;

$$m = \frac{(1) - (-2)}{\ln(14) - \ln(9)} = 6.79 \tag{7.5}$$

The Weibull modulus for slip cast alumina specimens is lower than that of alumina prepared using pressure slip cast counterpart. The pressure slip cast alumina specimens are both stronger and more reliable than the slip cast alumina specimens. A Weibull modulus of 10 to 20 is typical of the advanced ceramic materials. Unfortunately, in order to produce desired Weibull modulus, high purity raw materials and complex processing are normally required, making reliable ceramic parts expensive. But we saw from the results that we can reach good Weibull modulus values by using pressure slip casting method [55].

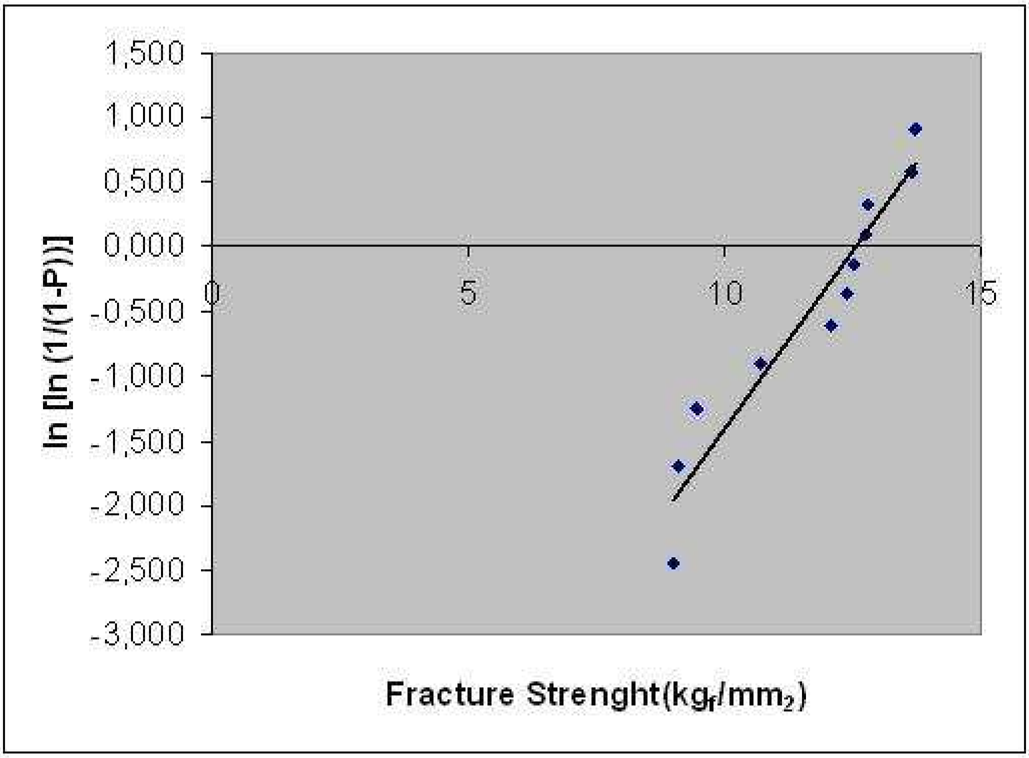

Figure 7.3. Fracture strength of the pressure slip cast specimens

7.3. Microstructural Investigation and Image Processing

JEOL/JSM-6335F (Scanning Electron Microscope) was used in micro structural examination seen from Figure 7.4 to Figure 7.11. These figures are the SEM micrographs of the specimens (Slip 2, sintered at 1600 °C) produced by both slip casting and pressure slip casting methods in this study. The particles have a sub-micron size. From the photomicrographs of Al_2O_3 compacts, it is understood that higher sintering temperature or longer time is needed to show better accuracy and higher mechanical stability.

From SEM micrographs, pressure slip casting seems to be more densely packed. The two methods presented a compact packing of particles. The pores are well distributed and are of 3 μm or less in size.

Image Processing Toolbox of Matlab was used to obtain the contour images. The images revealed the surface characteristics of the slip and pressure slip cast specimens.

Pores, edges and holes could be observed from the images.

The original SEM pictures were 1280 × 1024 pixels RGB images. First, images were down sized to 800 × 640 pixels. These pictures contained the SEM labels at the bottom as seen in the micrographs. To obtain a label free image, a 640 × 480 pixels rectangular section was taken. These images were flattened to a grayscale image in the Adobe Photoshop. Next step was thresholding the gray levels for revealing pores in the structure. For comparison, all images were threshold to a level of 40. These threshold images were then processed using the MATLAB Image Processing Toolbox. They were imported to MATLAB workspace and converted to binary images containing only ones and zeros. Total pixel size is simply found by multiplying 640 by 480. Then, the sum of all pixel values was taken. Since zeros contributed nothing to the sum, the result found was the sum of ones in the matrix. If this was subtracted from the total, number of zeros would be found. Percentage of pores in the structure could be calculated as follows:

$$total = 640 \times 680 = 307200 \tag{7.6}$$

$$ones = sum(Image) \tag{7.7}$$

$$zeros = total - ones \tag{7.8}$$

$$\%porosity = \frac{zeros}{total} \times 100 \tag{7.9}$$

Using the calculations above, the percentages of porosity values were evaluated and given in Table 7.7. The results showed that the pressure slip cast specimens have higher accuracy and have lower percentage of porosity than the slip cast specimens. Hence, higher compaction achieved in a pressure slip cast specimen is an advantage in terms of dimensional accuracy after sintering.

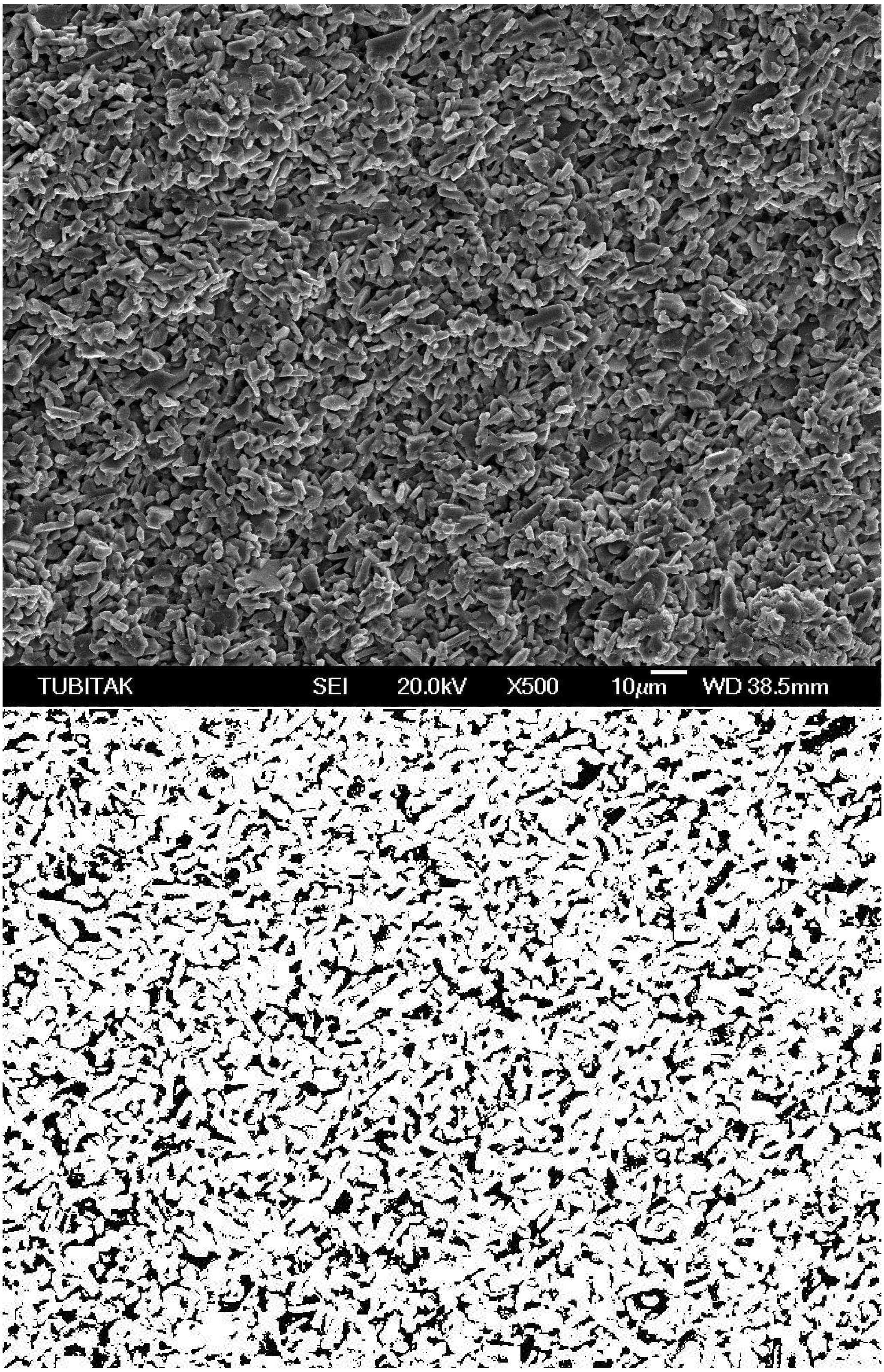

Figure 7.4. The image of the slip cast specimen (x 500)

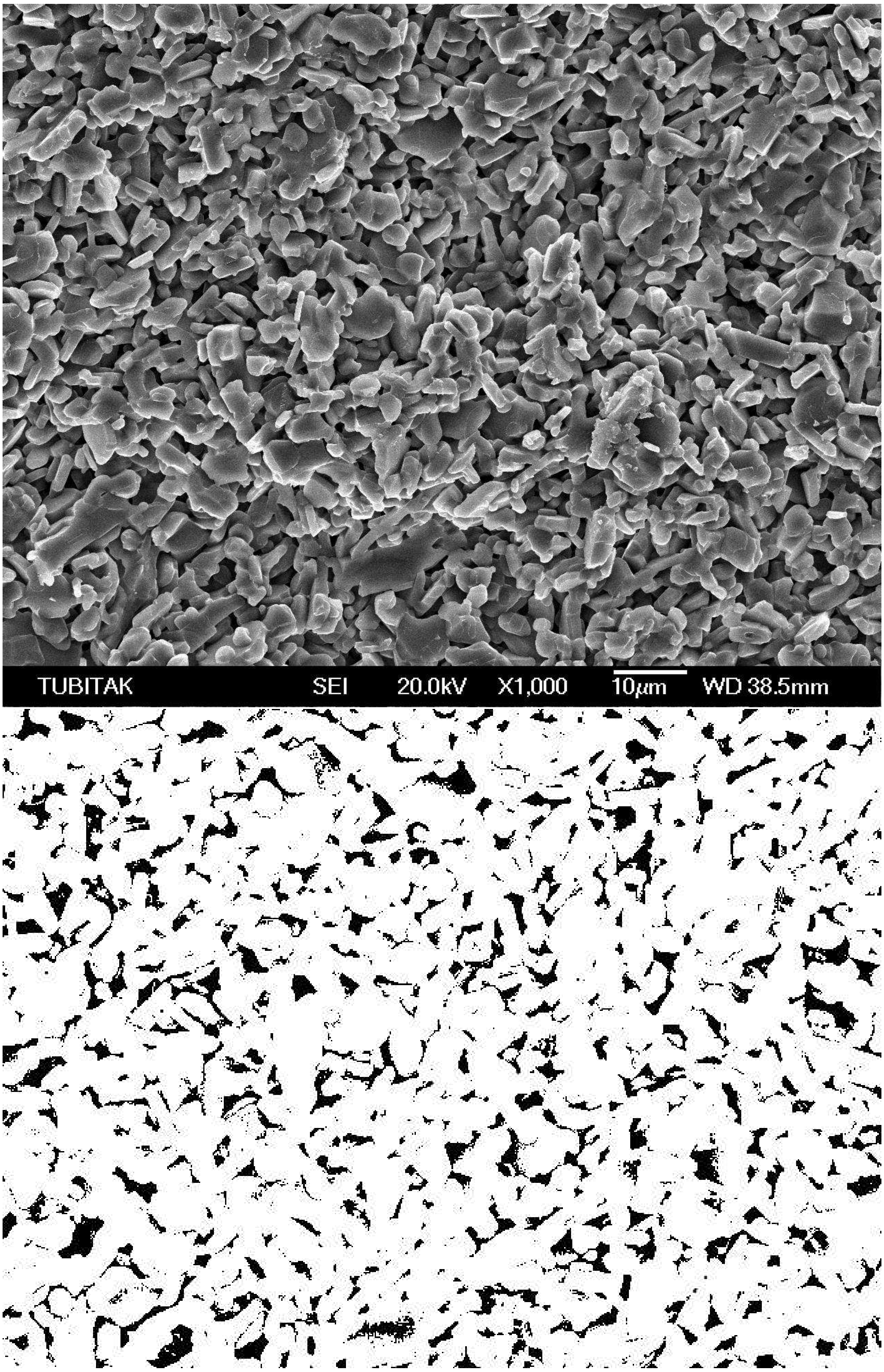

Figure 7.5. The image of the slip cast specimen (x 1000)

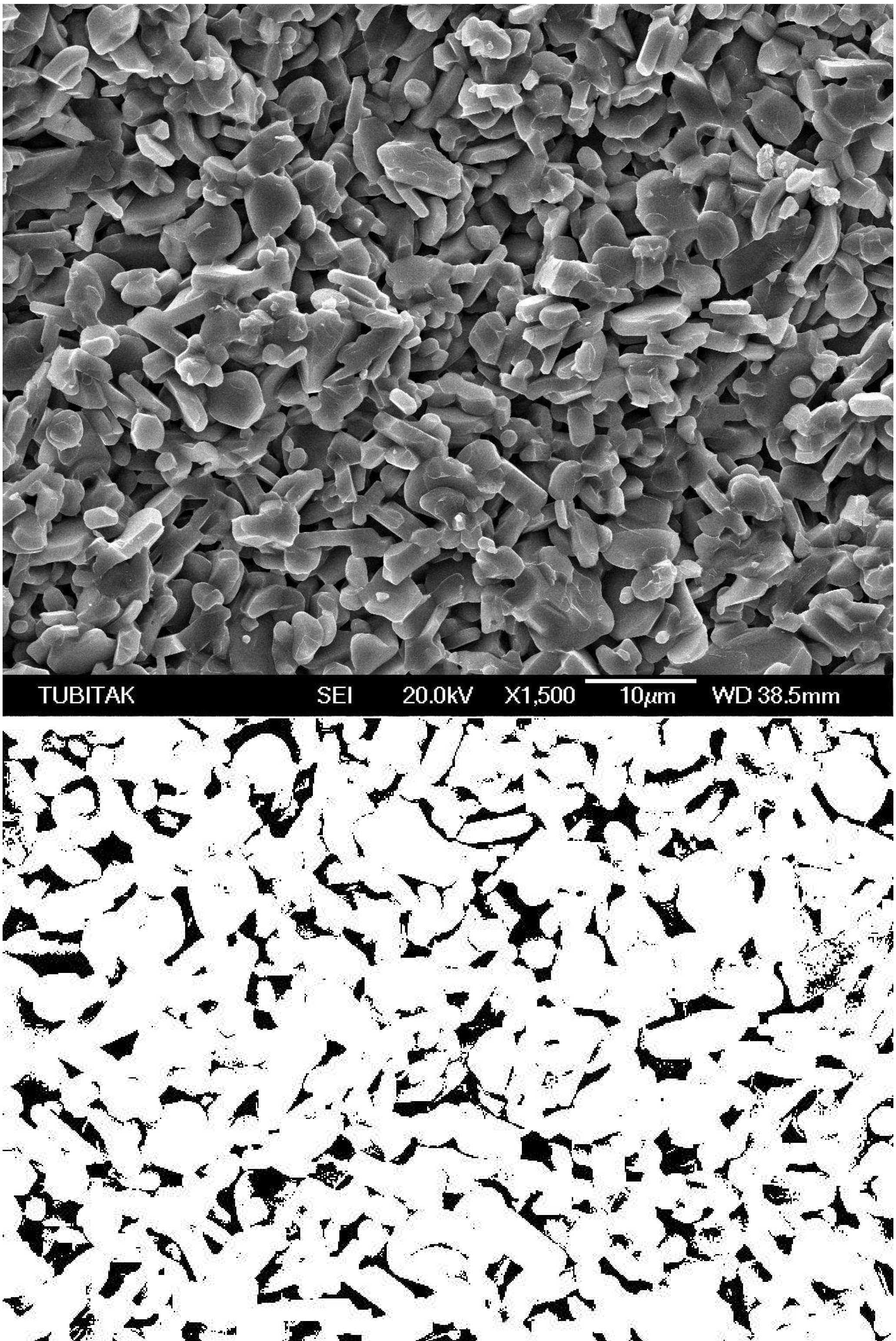

Figure 7.6. The image of the slip cast specimen (x 1500)

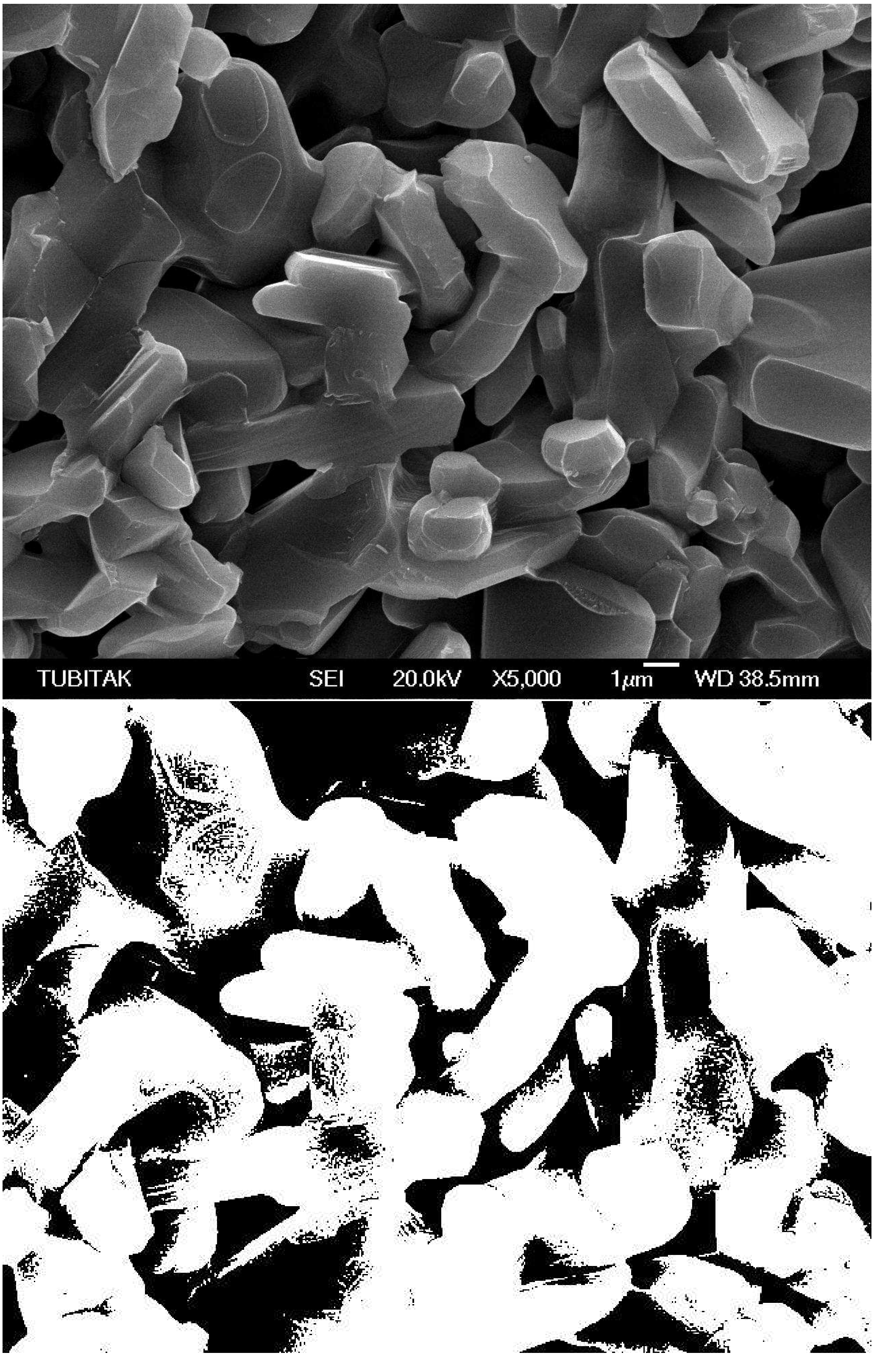

Figure 7.7. The image of the slip cast specimen (x 5000)

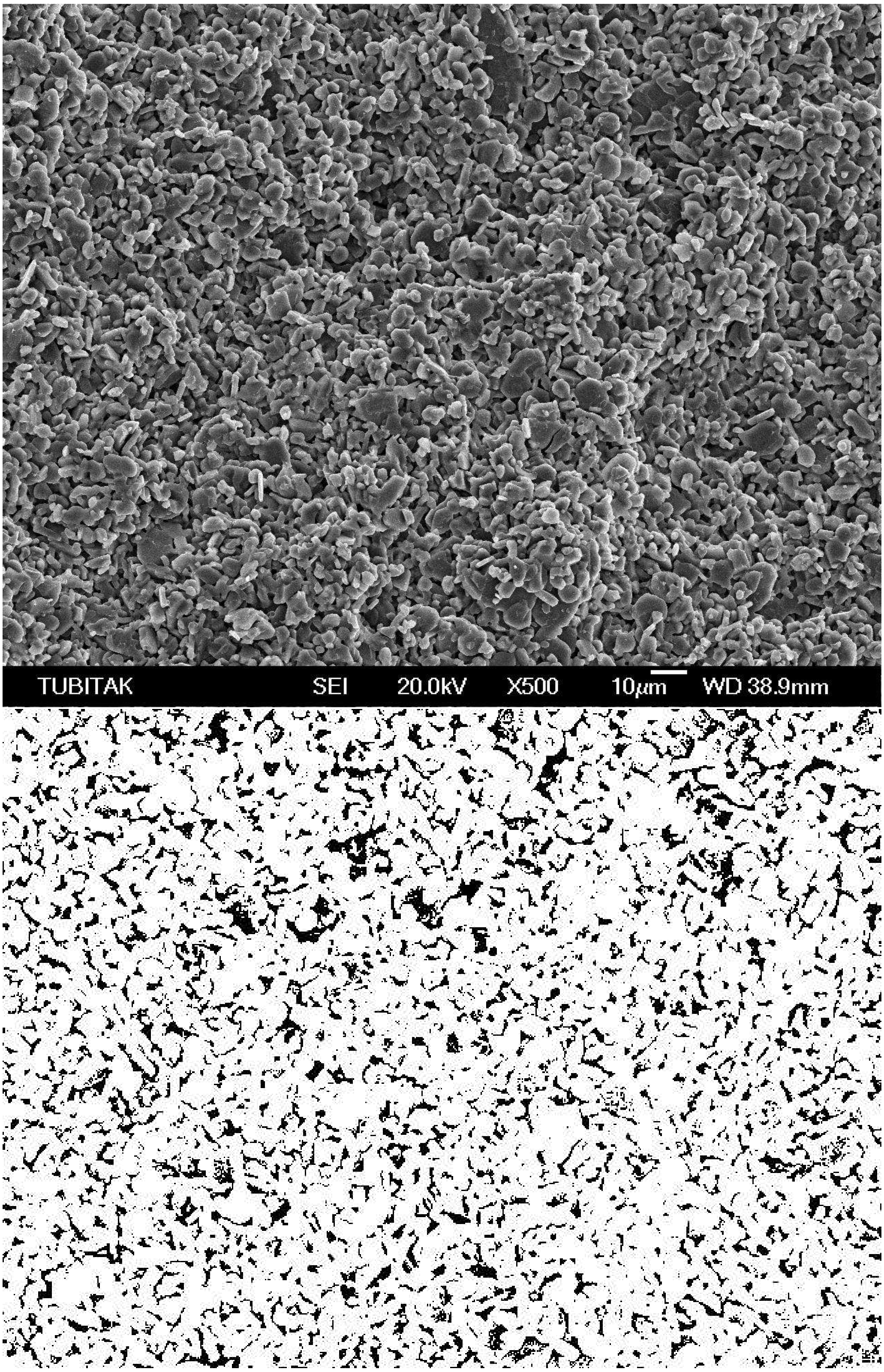

Figure 7.8. The image of the pressure slip cast specimen (x 500)

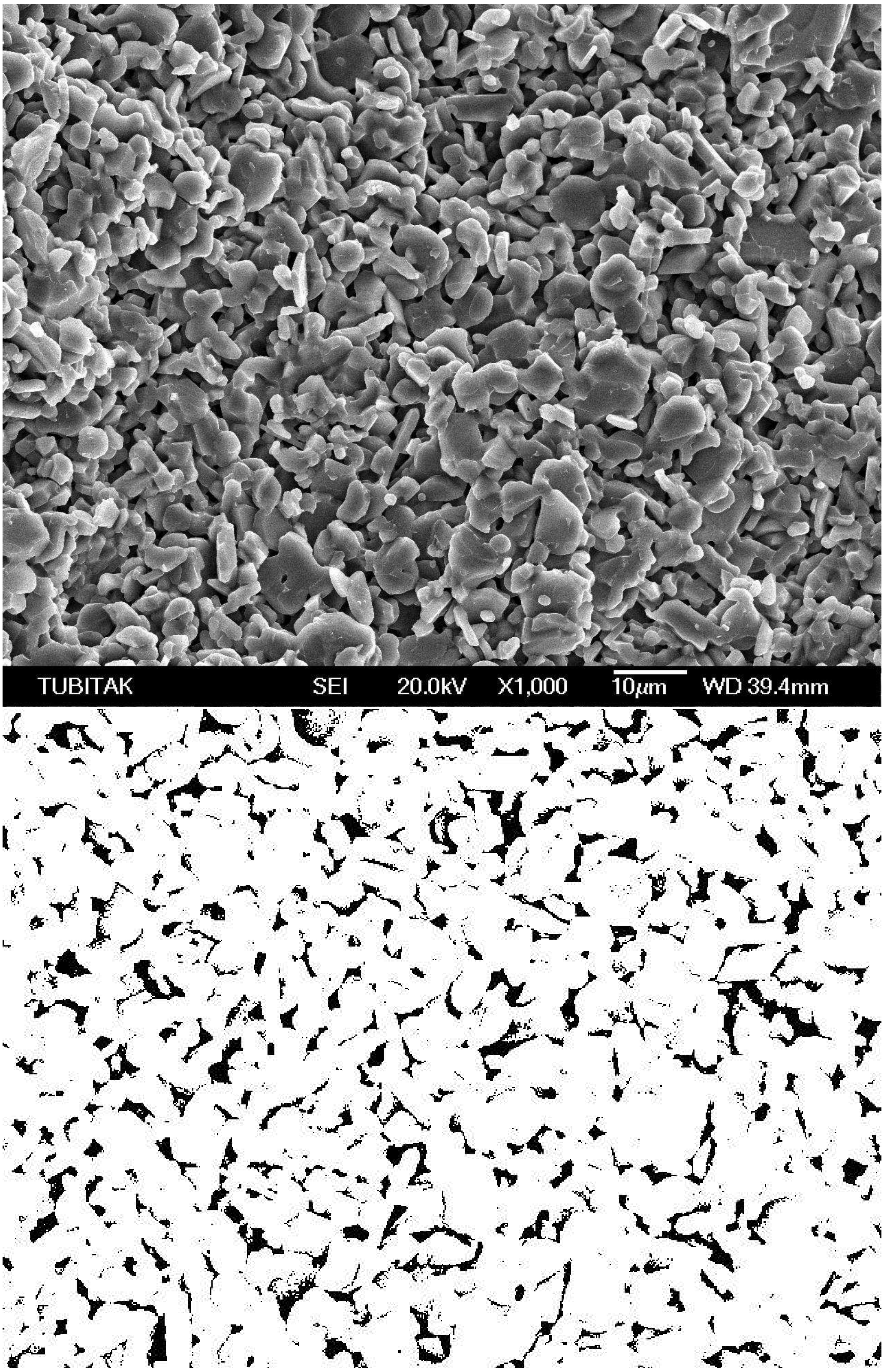

Figure 7.9. The image of the pressure slip cast specimen (x 1000)

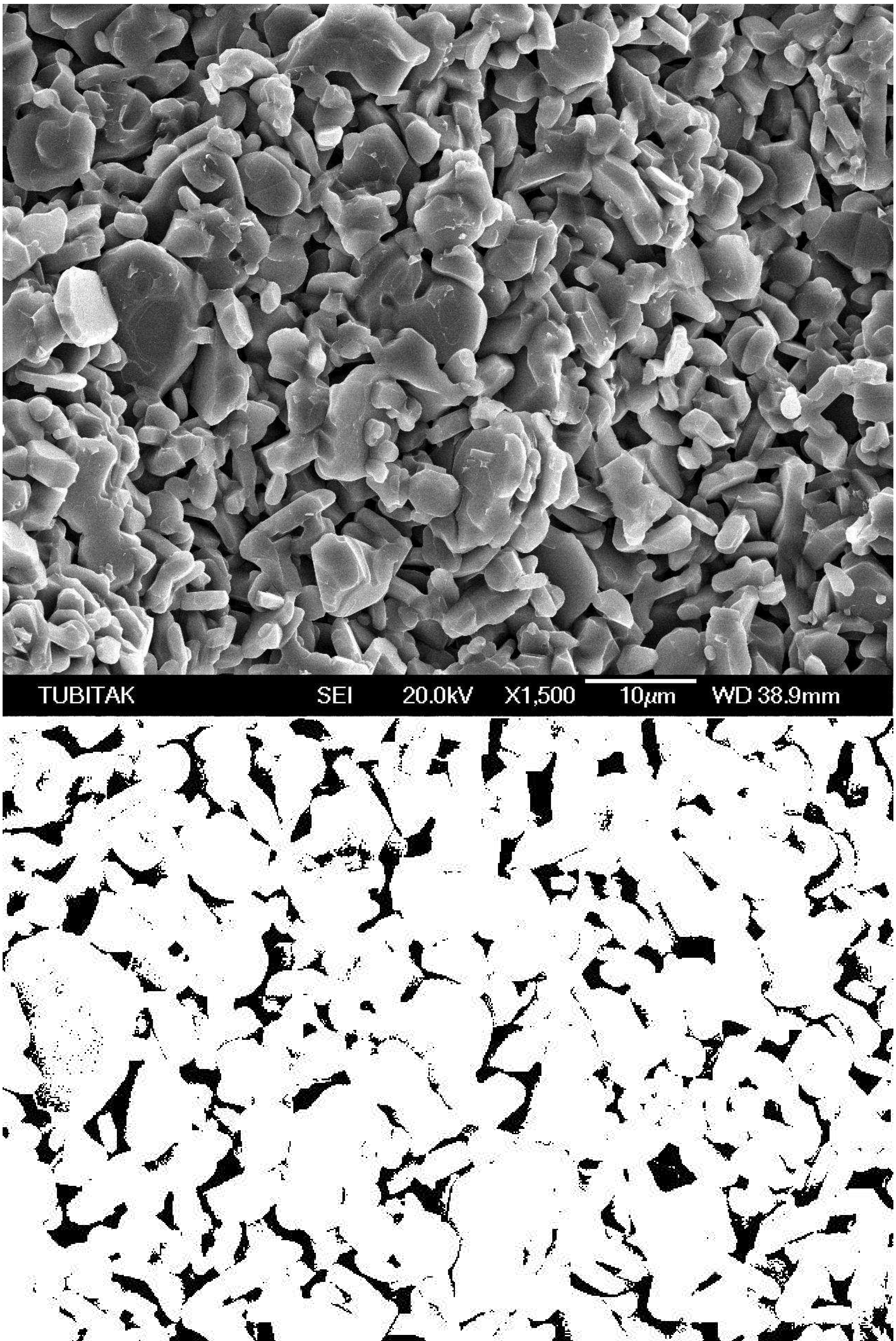

Figure 7.10. The image of the pressure slip cast specimen (x 1500)

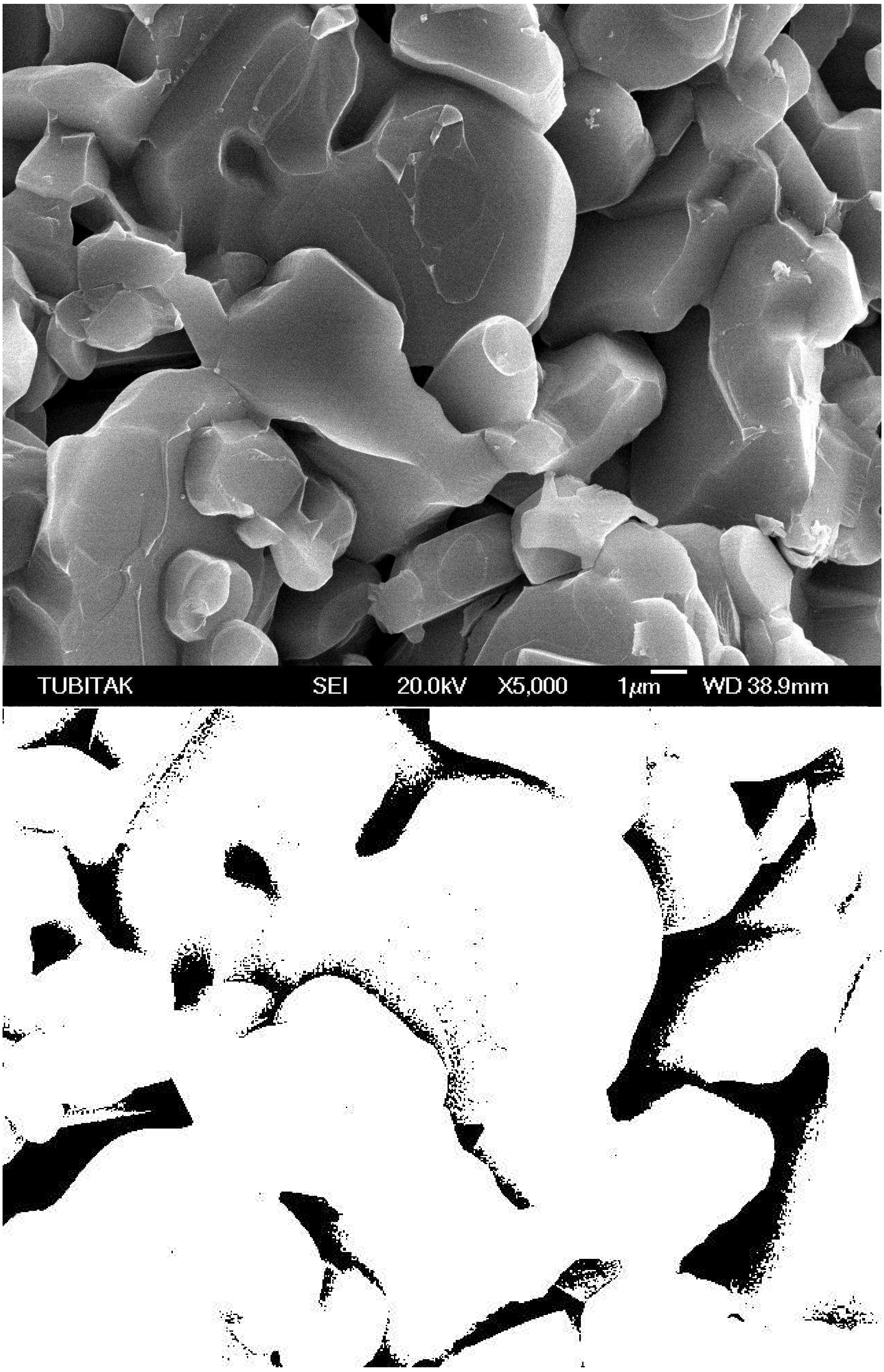

Figure 7.11. The image of the pressure slip cast specimen (x 5000)

Table 7.7. The percentage of porosity evaluated from the fracture surfaces at the slip and the pressure slip cast specimens (Slip 2, sintered at 1570^0C) from image processing of the micrographs

Image	Slip Cast Specimen (% Porosity)	Pressure Slip Cast Specimen (% Porosity)
x 500	23,36	16,73
x 1000	14,16	12,42
x 1500	16,53	14,12
x 5000	32,65	12,31

The percentage of porosity levels found from the image processing in Table 7.7 is somehow greater than those counterparts found from the bulk density measurements in Table 7.1 and Table 7.2. The reason of this result comes from the fact that the SEM micrographs is taken from the fracture surface of the specimens. A fracture surface contains more irregularities and does not necessarily represent the bulk material. Nevertheless, all of the results are supporting each other. It is concluded that the percentage of porosity values of the pressure slip cast specimens are smaller than those counterparts found from the slip cast specimens. This is in parallel with the higher mechanical properties and Weibull modulus values evaluated for the pressure slip cast specimens.

8. CONCLUSIONS

In order to understand the pressure slip casting method, two pressure casting set-ups were designed and then, manufactured. First one was mainly designed as an aluminium case and a stainless steel case. The second one was designed as Polyethylene case and a steel support. The process was further extended by producing a special ceramic mold for pressure application. For comparison, slip casting method was done also using a plaster of paris mold. The microstructure, strength, percentage of porosity and shrinkage were studied in the samples produced.

The most important issue appeared to be the slip preparation for the casting process. Slip casting was basically a filtration of water from the solid body consolidated at the mold surface. This solid body was demolded and dried. Finally, these dried castings were sintered. The samples machined from pressure slip castings provided higher mechanical properties and also Weibull modulus.

Experiments showed that, pressure casting kinetics is 20 times faster than slip casting one, then allowing the process scale-up to industrial productions. Furthermore, the use of pressure cast avoided the contamination derived from the plaster moulds.

Slip casting is a well-recognized method for the obtention of dense ceramic parts. On the other hand, pressure slip casting has many advantages for complex parts in large scale fabrication. It was observed that the higher applied pressure caused the faster wall thickness formation rate. Hence, increased casting rate in pressure slip casting improved productivity. In addition, pressure slip casting promoted more homogeneous distribution of ceramic particles in the cast body.

APPENDIX A: TECHNICAL DRAWINGS OF THE ALUMINIUM PRESSURE SLIP CASTING SET-UP

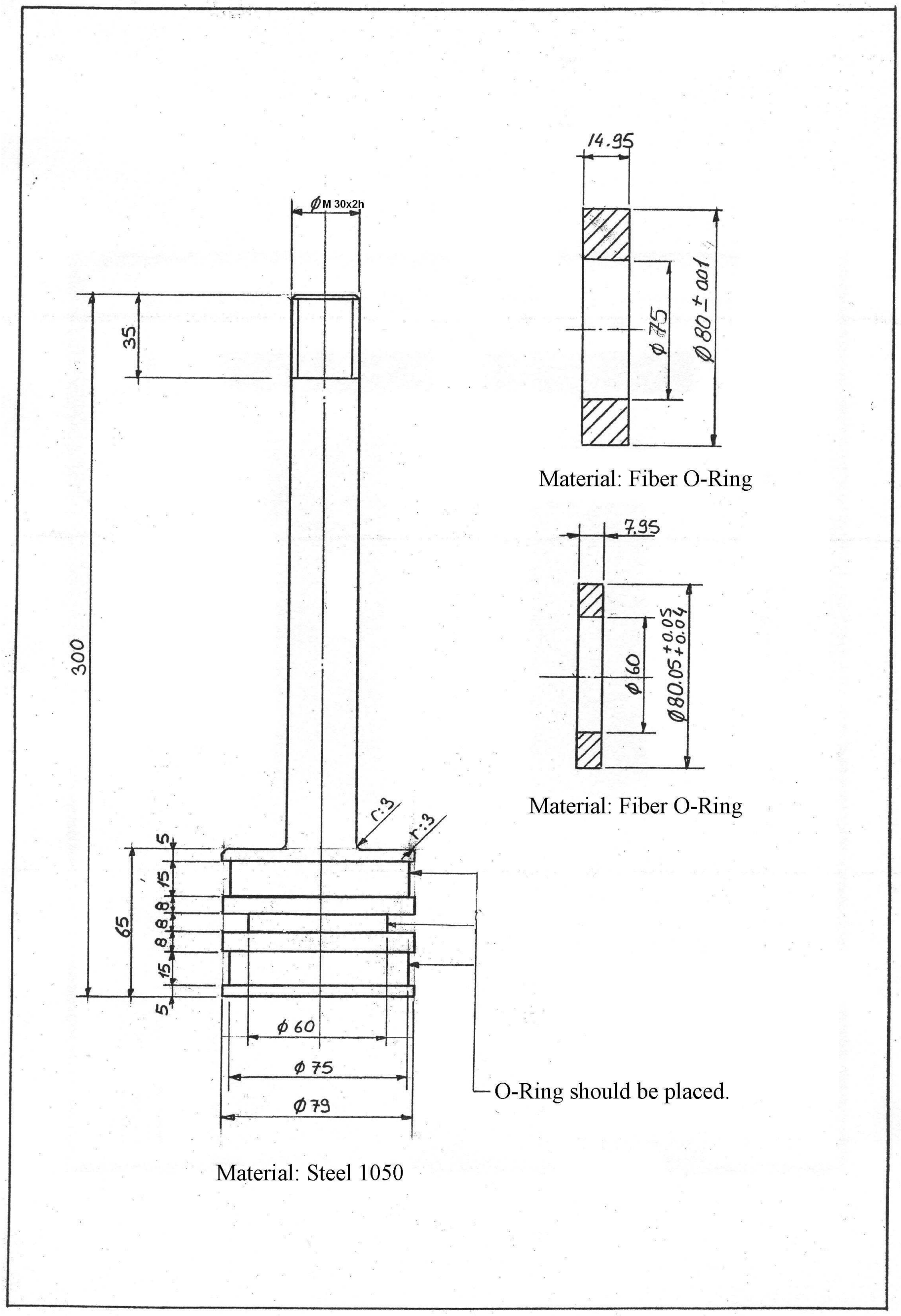

Figure A.1. Technical drawing of piston for pressure slip cast set-up

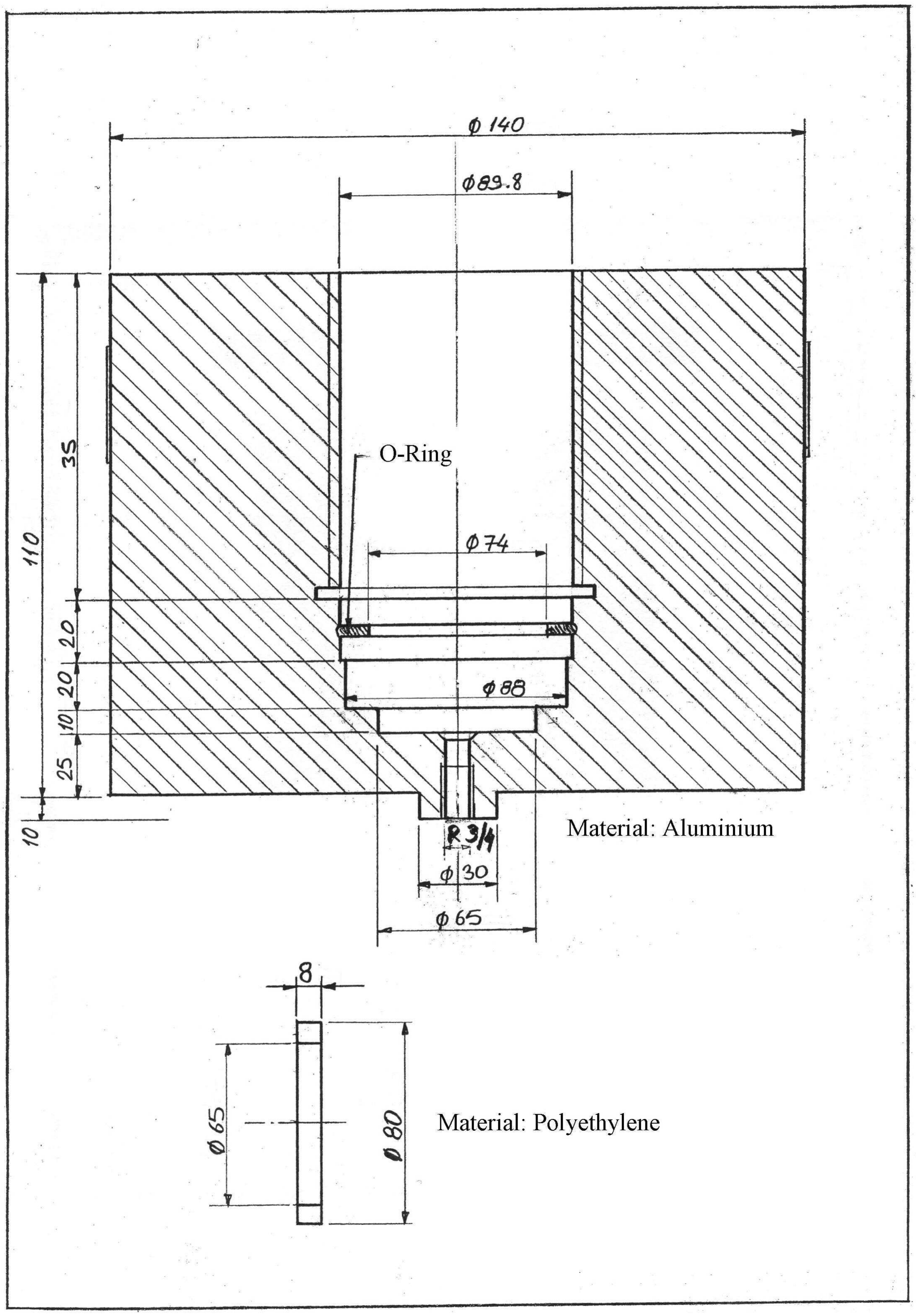

Figure A.2. Technical drawing of bottom case for pressure slip cast set-up

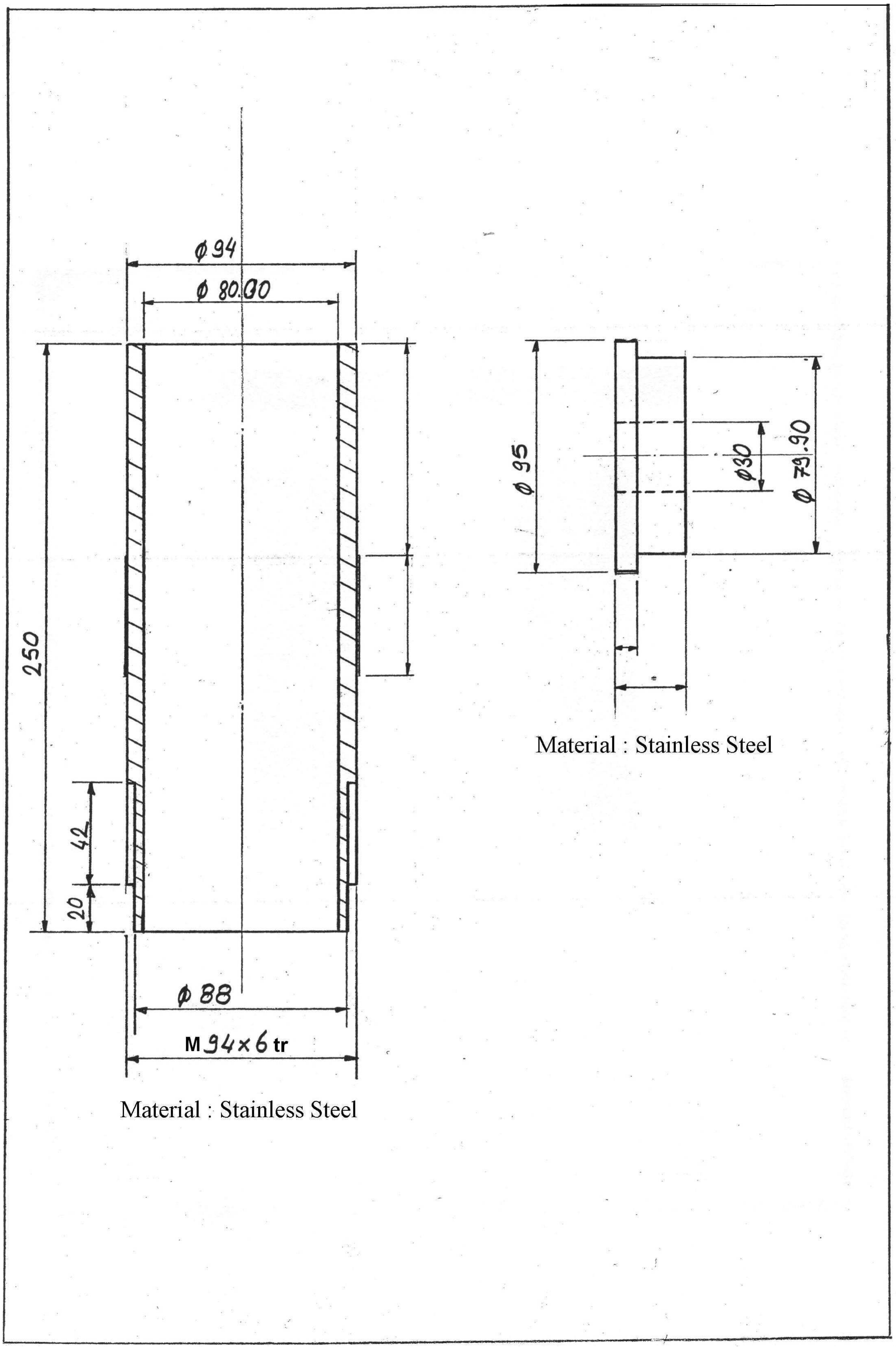

Figure A.3. Technical drawing of chamber for pressure slip cast set-up

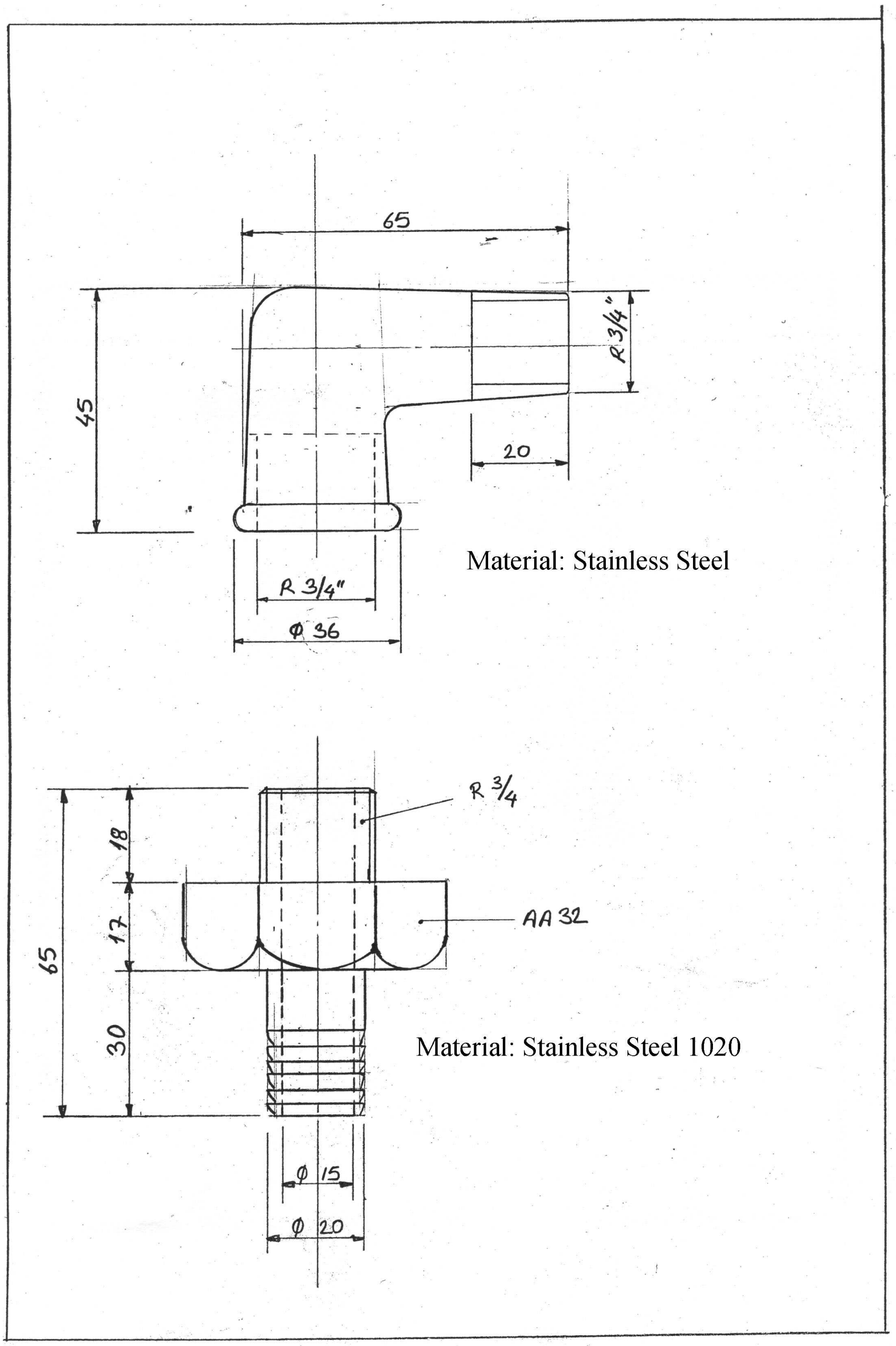

Figure A.4. Technical drawing of pipes for pressure slip cast set-up

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