IMPROVED SOL BASED CERAMIC MOULDS FOR USE IN INVESTMENT CASTING

by

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1st of 3 files

Introduction and chapters 1-2
The remaining chapters
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SYNOPSIS

An investigation has been carried out into the mechanisms of failure of silica bonded investment casting moulds, with the aim of reducing failure rates for larger components. The analysis begins with a detailed microstructural examination of a current commercial mould system using scanning electron microscopy and other allied analysis techniques. The mould structure is shown to be non-uniform and unpredictable, with poor packing of the ceramic constituents leading to a non-uniform porosity network. The structure and distribution of the binder is also established and this indicates that the major load bearing points within the mould consist of thin areas of silica. As such, the overall performance of the mould is directly related to that of the silica itself. This binder is shown to contain impurity elements leached from the ceramic filler at various stages during mould manufacture. These elements alter the phase composition and thermal properties of the binder.

Mould temperature profiles for a range of casting sizes have been measured and used to illustrate the relationship between metal weight and maximum temperature attained within the mould section. The profiles are also used to investigate the creep response of silica based binders. It is found that a combination of high temperatures and creep within the silica phase is responsible for the casting defects found with larger components. From these observations, a prediction is made regarding failure mechanisms and suggested remedial action. The thermal properties of several commercial water based binders are evaluated and the suitability of each as an alternative binder is discussed.

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DEDICATION

To my wonderful husband for help, encouragement and the constant reminder that the mortgage has got to be paid. Special thanks go to my family, whose unswerving dedication to put me in a mental institution before my time, has helped me to put the PhD in its true perspective.

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GLOSSARY OF TERMS

Air-dried	Mould dried in air, without the application of heat
Assembly	A group of patterns on sprue and runner for casting purposes
Autoclave	Equipment for the removal of wax using steam under pressure
Back-up	Coarse grained refractory material used to surround the mould to impart physical support during casting
Back-up coat	The ceramic slurry or dip-coat which is applied in multiple layers following the first dip-coat to provide a ceramic shell of the desired thickness and strength
Binder	Liquid or solid additive used to bond refractory particles
Bulging	Movement of the mould wall during casting which produces a metal surface which is concave instead of flat
Burn-out	Firing a mould at high temperature to remove the pattern material inside.
Ceramics	Refractory material usually based on alumino-silicate, fused silica or zircon mixtures
Cire-Perdue	French term for the lost wax process
Core	1. A metal insert in a die to produce a hole in a pattern 2. Wax core - soluble wax shape used to produce internal geometry of patterns 3. Ceramic core - preformed refractory aggregate inserted in wax pattern to shape the interior of the casting 4. Collapsible core - a metal insert made in two or more pieces to permit withdrawal from an undercut mould surface
Core cavity	The cavity produced in a casting by the use of a core
Cut off	Removing casting from sprue by refractory wheel or saw, arc-air torch or gas torch
Deoxidation	Removal of excess oxygen from the molten metal, usually accomplished by adding materials with a high affinity for oxygen
De-waxing	The process of removing the expendable pattern from the investment mould
Die	The metal form from which the expendable patterns are made
Dip coat	1. In the solid mould technique: an extremely fine ceramic coating applied as a slurry directly to the surface of the pattern 2. In the shell mould technique: an extremely fine ceramic coating which is applied to the pattern by dipping into a ceramic slurry
Ethyl-silicate	A strong bonding agent for sand and refractories which deposits silica upon drying from a solution. Also known as tetraethyl silicate or TES

Feeder	A reservoir of molten metal to compensate for contraction of the metal as it solidifies, thus preventing voids in the casting
Fired mould	Shell mould which has been heated to a high temperature in order to develop the bond between the refractory particles
Filter	Usually of ceramic, the filter is placed at the entrace to the mould cavity to remove inclusions and slag from the liquid metal
Flash dewaxing	Sudden application of heat to a shell mould for dewaxing
Gas porosity	Dispersion of fine cavities in the metal resulting from liberation of gas during solidification
Gating system	The cavities in a mould made from a complete assembly of sprues, runners and gates through which molten metal flows to the pattern cavity
Grain refiner	Any material added to a liquid metal for producing a finer grain size in the subsequent casting
Grit	Crushed ferrous or synthetic material used in abrasive blasting equipment for cleaning of castings
Heat treatment	A combination of heating and cooling operations carried out upon the casting in order to produce the desired (improved or stabilised) metal properties
Hot tear	Surface discontinuity or fracture caused by either external loads or internal stresses or a combination of both acting on a casting during solidification, and subsequent contraction at temperatures near the solidus
Inclusions	Particles of slag, refractory materials, sand or deoxidant products trapped in the casting during solidification
Knock-out	Removal of the ceramic shell from around the metal casting
Microporosity	Extremely fine porosity caused in castings by shrinkage or gas evolution
Pattern	A form of wax-base or plastic-base material around which the ceramic shell is formed
Pattern injection	The process of filling the pattern die with molten pattern material under pressure
Permeability	The property of a material which allows the passage of gas through the structure
Raining	The process by which stucco material is applied to the ceramic shell
Riser	A reservoir of molten metal provided to compensate for internal contraction of the casting during solidification
Scab	Rough surplus of metal on a casting caused by removal of primary mould material during pattern removal

Slurry	A flowable mixture of refractory particles suspended in a liquid
Stucco	Coarse refractory material used to minimise drying stresses in coatings, build up mould bulk and provide a rough keying surface to facilitate the application of further slurry coats
Stuccoing	The application of granular refractory to the surface of the wet dipcoat

CHAPTER ONE

1.1: The History of Investment Casting

Investment casting, popularly known as the 'lost wax' or 'cire perdue' process, has a history which reaches far back into time. Archaeological investigations reveal that Early Man employed the principle to produce metal tools[1] and the Chinese to cast bronze statues before 4000BC[2]. Early Greeks cast monumental bronzes, and sculptures from West Africa reveal cast portrait heads over cores made of clay and manure[2]. Aboriginal Quimbaya goldsmiths from Columbia[3] were known to produce detailed and intricate cast gold figures by lost wax techniques. At the same time Aztec gold workers developed a difficult and involved technique for producing high quality jewellery[3]. Reapplication of the technique in modern times is attributed to the sculptor and artist Benvenuto Cellini who produced many cast works of art during the 16th Century[2].

Although the process was used successfully for thousands of years, it was not until the late 19th Century that a more widespread application was developed. In 1897, an American Dentist began to produce gold inlays and fillings for false teeth using the technique. Jewellery manufacturers soon realised that the same principle could be extended to make intricate gold shapes possessing fine detail and smooth surfaces.

Though used extensively for dental and ornamental applications, no serious effort was made to produce industrial castings until 1932. In this year a series of highly corrosion resistant cobalt-chromium alloys (Vitallium)[4] were developed by the Austenal Laboratories for the production of prosthetic devices. As these alloys could not be forged or machined, a variation of the investment technique called the 'block mould' method was developed allowing orthopaedic and dental components to be cast. The method involved placing a solid mould around a wax pattern and filling the space with a slurry made from refractory ceramic and sodium silicate to produce a ceramic mould[5].

No significant attention was paid to the process until 1939, when the advent of World War 2 created an urgent demand for finished components from the machine-tool industry. An alternative route of manufacture was needed to to speed up the supply of precision components to the arms and aircraft industries. The block mould process was adopted to produce turbine blades and other components such as turbo-superchargers which allowed bomber and fighter aircraft to fly at higher altitudes. Thus, the process was adapted for the production of engineering castings from certain metals which do not readily lend themselves to machining or forging.

In 1950 most investment foundries were exclusively producing components for aircraft engine and military applications by the block mould process[5]. Though successful, the process was labour intensive and time consuming. At this time another technique called the Shaw Process was developed using an ethyl-silicate binder and an alumino silicate refractory material. The technique was less labour intensive but not flexible in the choice of component since it used a reusable pattern made of plaster, wood or metal.

Increased demand for cast components, the awareness of the importance of the mould surface and the 'supportive role' of the refractory material led to the development of the ceramic 'shell'. An investment shell is a monolithic mould formed by dipping of a disposable pattern into a refractory slurry to build up the required thickness before the pattern is removed. The first shell process to be developed in 1949 was the Mercast Process[6] in which a frozen mercury pattern was coated with a specially formulated slurry. After that a series of ceramic shells were developed using different pattern, refractory and binder materials by methods such as the Investment 'X' Process(1952) and the Glascast Process (1957).

In 1960, the Monsanto Chemical Company introduced the first of a series of rapid-set silica binders which significantly increased the rate of mould production[1]. Subsequent mould compositions polarised into four main types:

1. Colloidal silica sol bonded primary coat (air-dried) followed by secondary coats bonded by ethyl-silicate (air-dried and gelled with ammonia).

2. All coatings bonded by colloidal silica sol and set by air-drying (with or without chemical setting).

3. The alternate use of acidic and alkaline slurries.

4. All coatings bonded with ethyl-silicate (air-dried) and using quartz refractory.

Rapid-set binders also allowed the investing of the wax pattern to be mechanised. By 1969 several companies had introduced robots or ceramic moulding machines for the various dipping and coating operations. These early machines had a payload capacity of 65 kg. The 1960's process has since been rationalised and improved by using greater process control but very few developments in the structure or composition of the shell mould have been made, illustrated by the fact that most foundries still use one of the binder systems identified above.

The major trends in process development are summarised in Figure 1. At present most investment foundries have fully automated wax pattern and ceramic mould production facilities. The capacity of some mould dipping robots has increased to 350 kg making it possible to manufacture even larger castings. Various alloys such as aluminium, steel, titanium, nickel and cobalt are air or vacuum cast on a regular basis. The continuing need to expand and develop the process has led to specialised techniques such as Directional Solidification and Single Crystal Casting. Alternative processes such as Replicast[2], and more recently the Lost Foam process[5] have been developed to compete with the investment process. These have tended to become specialised and have found their own niche markets and as such, do not seem to be seriously affecting the investment market.

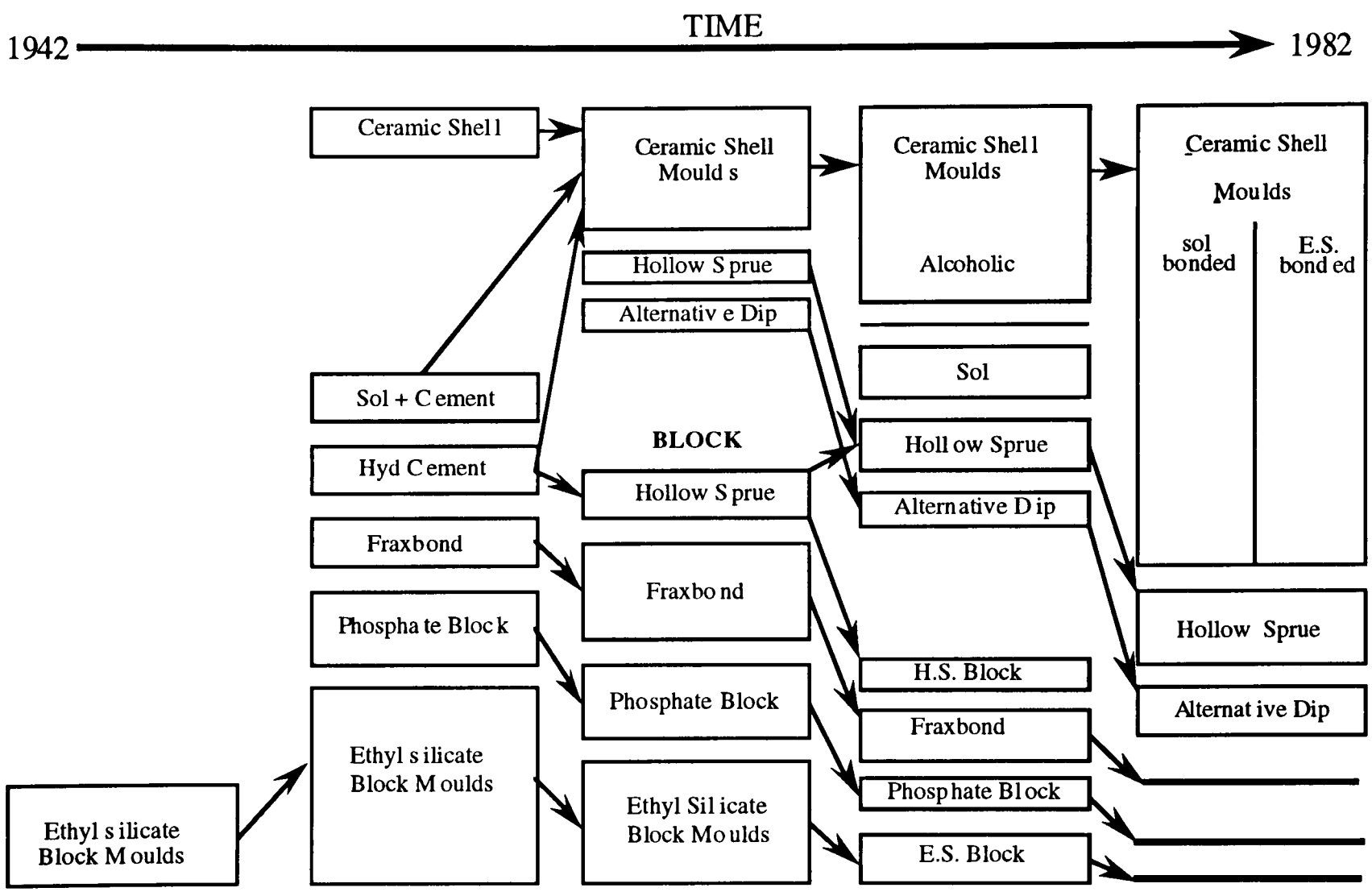


Figure 1: Major trends in process development[1]

1.2: The History of Deritend Precision Castings

In Germany, during the Second World War, three allied prisoners of war met in a POW camp and became firm friends. Captain John Humphries, Major Bob Danielson and Captain Robinson began to read Red Cross books sent over to entertain the prisoners, especially those that detailed new

engineering processes such as investment casting. The idea to begin a company of their own was formed and upon their return to England they set about finding suitable premises. Major Danielson's father owned many engineering firms and gave the trio permission to use an old stable block at Deritend Stamping Company which was sited in an outlying district of Birmingham. Thus, in 1947, Deritend Precision Castings was formed with an initial workforce of 10 people. By 1953 the workforce had risen to 24 and the stable block could no longer accommodate the volume of work that was required to meet the ever growing order book. In this year the entire factory was transferred to its present site at Vines Lane, Droitwich, Worcestershire. With the help of a Government scheme new premises were designed and built at the site which runs alongside the railway line and the old Roman Road.

The site expanded over the next thirty years until in 1982 there were three specialised investment foundries for Aircast steel, Aluminium and Vacuum cast steel. Following an extensive rationalisation programme in 1983, three commercial foundries in Scotland, Somerset and Roscommon were created. After the retirement of several directors, Deritend became part of the Christy Hunt Organisation in 1987. This partnership lasted for only twelve months and in 1988 the company became part of the Triplex Lloyd Group. The Aircast and Vacuum cast foundries have since been merged and extensive redevelopment of the site has resulted in the present site being four times the size of the original foundry with plans for further expansion. The process has been fully automated with Deritend recently commissioning one of the largest ceramic shelling robots in Europe. A wide range of components are cast for Aerospace, Defence, Power and Orthopaedic applications.

1.3: The Principles of Investment Casting

The investment casting process involves the production of engineering castings using an expendable pattern. There are two basic methods employed; block mould production and ceramic mould production. Since shell moulds are generally more economic in their use of raw materials and much more flexible as regards the size and weight of the castings that can be produced, the majority of investment castings are now made by this method.

The basic steps in the production of an investment cast component are shown in Figure 2. A metal die is used to produce a component pattern. A complex blend of resin, filler and wax is injected into the die under pressure. As the quality of the finished casting depends critically upon the wax, most casters use wax that has been specifically designed for the application. The dies are made from materials such as duralumin or brass to reduce tooling costs. The solid patterns are then assembled into a cluster and mounted onto a wax runner system. The runner system comprises a series of passageways and reservoirs that not only guide liquid metal into the main cavity but also provide additional liquid to compensate for cooling contraction.

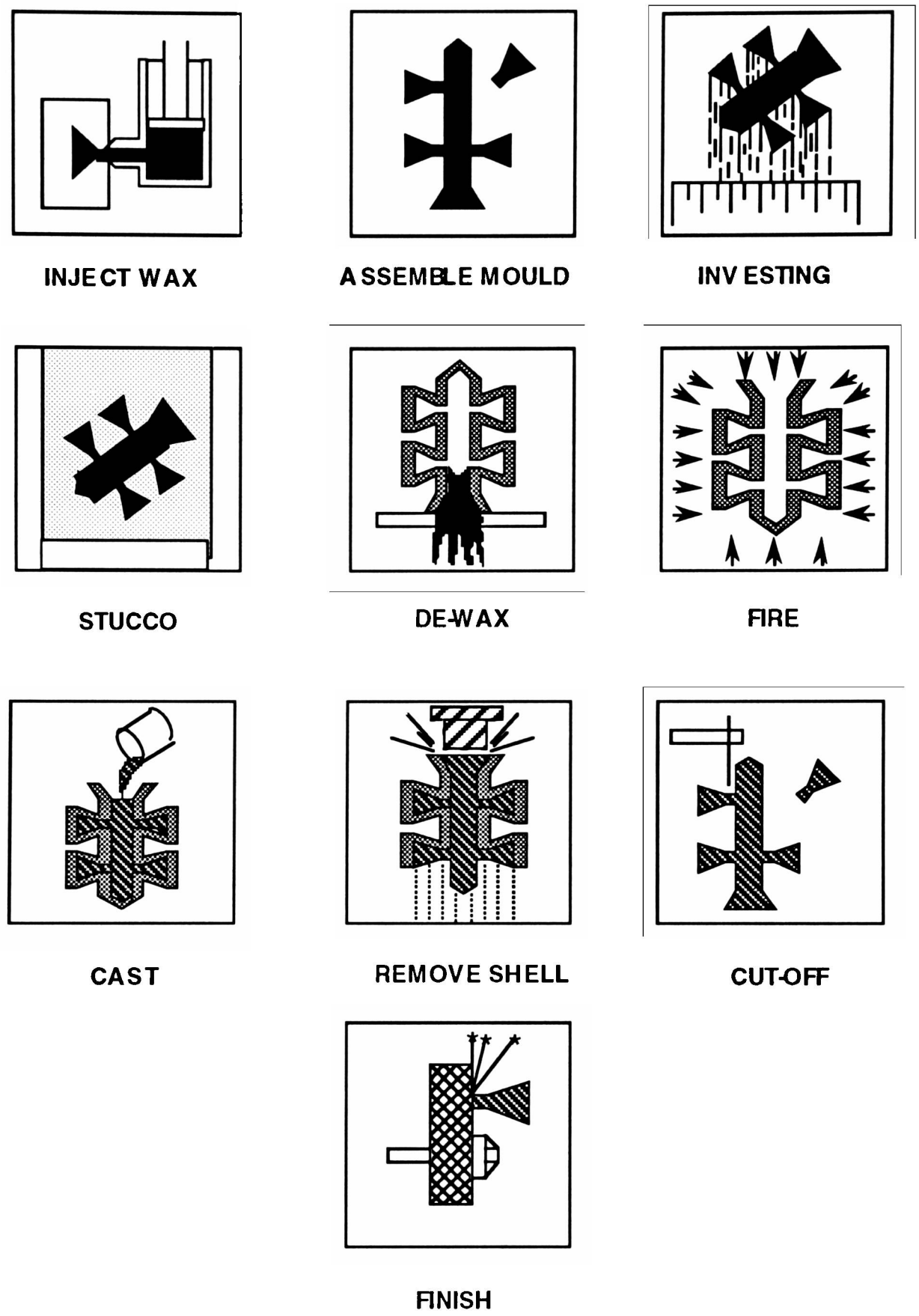


Figure 2: Illustration of the principles of investment casting

The covering of a wax assembly with a refractory material is known as investing which gives rise to the modern name for the process. The wax assembly is dipped into a thin refractory slurry consisting of a liquid binder and a refractory powder. After draining, grains of refractory (stucco) are deposited onto the damp surface to produce the primary refractory coating. The purpose of the stucco is to minimise drying stresses in the coatings by presenting a number of stress concentration centres which

distribute, and hence, lower the magnitude of the local drying stress. The second main purpose of the stucco is to present a rough surface, thus facilitating a mechanical bond between the primary coating and the back up or secondary investment. When the primary coat has set (air-dried until the binder gels) the assembly is systematically dipped into a secondary slurry and stuccoed until the required thickness of shell is built up. The particle size of the stucco is increased as more coats are added to maintain maximum mould permeability and to provide bulk to the mould. Each coating is thoroughly hardened (usually chemically set and then air-dried) between dippings. Thus an investment casting mould consists of individual layers of fine refractory material and granular refractory material held together by a binder which has been set to a rigid gel.

After drying, the wax pattern material is removed in a steam autoclave, where the shells are subjected to steam at high temperature and pressure. Heat is transferred rapidly through the shell causing the wax to melt and drain away. The cavity left behind is an exact replica of the original pattern. The mould is then fired at a high temperature to remove any residual wax and to develop the bond strength of the binder. Metal can be poured into the mould whilst still hot or more usually the mould is allowed to cool and reheated to firing temperature before casting. Melting and casting under vacuum is frequently used for high temperature alloys where avoidance of contamination by oxidation products is critical. The range of alloys which can be investment cast is wider than that for any other single manufacturing process. Listed below are some of the alloy types that are regularly used to produce engineering castings[4]:

carbon steels
high and low alloy steels
stainless steels
nickel-base alloys
cobalt-base alloys
grey cast iron
spheroidal graphite cast iron
alloy cast iron
titanium alloys

copper
bronzes
brasses
aluminium bronze
silicon bronze
beryllium copper
aluminium alloys
magnesium alloys

When the metal has cooled sufficiently the mould material is removed by impact, vibration, grit-blasting, high pressure water blasting or chemical dissolution to leave the castings which are mechanically cut from the runner system. Various post-casting operations such as heat treatment, hipping or surface coating may be carried out to meet the customers requirements. Often the components undergo rigorous evaluation using a series of NDT techniques, especially for aerospace applications.

1.4: Key Requirements of the Ceramic Mould

The key requirements of an investment casting mould are;

1. Sufficient green (unfired) strength to withstand wax removal without failure.

2. Sufficient fired strength to withstand the weight of cast metal. Excessive strength must be avoided as this hinders the cooling contraction of the metal and produces hot tears or cracks within the casting (as the metal cools it shrinks and if the mould walls are rigid then localised stress concentrations build up which are relieved by fractures).

3. High thermal shock resistance to prevent cracking during metal pouring

4. High chemical stability so that individual components do not break down at high temperatures or prolonged durations at high temperatures.

5. Low reactivity with the metals being cast to improve the surface finish.

6. Sufficient mould permeability and thermal conductivity to maintain an adequate thermal transfer through the mould wall and hence allow the metal to cool.

7. Low thermal expansion to prevent dimensional changes within the mould wall and ultimately the casting.

8. Ability to remove the ceramic material from the casting after metal solidification and cooling.

1.5: Advantages of the Process

The investment casting process has several unique advantages that few alternative metal forming techniques can offer:

1. Castings can be made in an extensive range of metal alloys both ferrous and non-ferrous. Many of the alloys used are extremely difficult or even impossible to shape or form by any other manufacturing route. The process is particularly suited to the casting of heat resistant nickel or cobalt based alloys with which exceptionally good finish and metallurgical quality can be achieved.

2. Complex shapes which would be uneconomical or impossible to produce by machining or weld fabrication are easily cast using the investment process.

3. Enhanced mechanical properties can be tailored to requirements using suitable heat treatments.

4. Tooling is relatively cheap and is adaptable to change or modification. This adaptability allows castings to be produced in large quantities and also in small numbers for development trials prior to full production runs.

5. A high degree of dimensional accuracy and excellent surface finish can be achieved even throughout long production runs. General tolerances of ± 0.13mm per 25mm are usually quoted but the range is dependent upon the size and geometry of the component.

6. Production costs are competitive with other techniques due to substantial savings on raw materials and labour costs. Finishing costs are less since only a small amount of or even no machining is required to achieve high precision dimensions. Overall capital investment is reduced.

7. Component shaping is aesthetic and uniform since a one piece mould without a joint line is used. The need for draft angles is eliminated.

8. High casting integrity is always achieved.

9. Economic weight savings are achieved since sound strong sections thinner than 1.6mm can be cast.

1.6: Disadvantages of the Process

1. The process is time consuming and labour intensive.

2. There is a limit to the weight and size of components that can be produced both in terms of manual handling of waxes and maximum capacity of the mould dipping robots.

3. Alloys which are highly reactive, such as titanium, cannot be cast into refractory moulds.

4. As a casting process, most components require heat treatment to modify grain structure.

1.7: Future Developments

At present, the UK investment casting industry has an annual turnover of approximately £250 million (Figure 3), with an estimated future growth rate of 5 - 7% per annum[5]. With continued commitment to quality and research the industry should continue to expand well into the next century and beyond. Developments in the next few years are likely to include[8,7]:

1. The use of bigger moulds to produce large monolithic components as an alternative to complex assemblies fabricated from individual parts.

2. More widespread automation, including the use of robots, to improve the consistency of shell formation and casting quality.

3. Continued interest in the better control and understanding of the basic casting processes to produce reproducible castings under economic production conditions.
4. A greater use of semi-empirical techniques such as modelling of metal solidification to improve casting design and allow the use of CAD/CAM* manufacturing techniques.

5. The development of processes to cast new materials such as metal-matrix composites and advanced aluminium alloys for the aerospace industry.

6. Increased use of directional solidification and single crystal techniques for the production of equiaxed castings (turbine blades) and thin-wall components.

1.7: Introduction to the Project

Investment casting allows dimensionally accurate components to be produced in high or low volumes - a much cheaper alternative to forging or metal turning since the waste material is kept to a minimum. With increases in the labour and machining costs associated with conventional metal fabrication methods, the economic incentive for using the investment casting technique for the production of progressively larger components has increased. The introduction of mechanisation (robots) has promoted an increase in the weights of castings being routinely produced by foundries.

* CAD = computer aided design CAM = computer aided manufacture

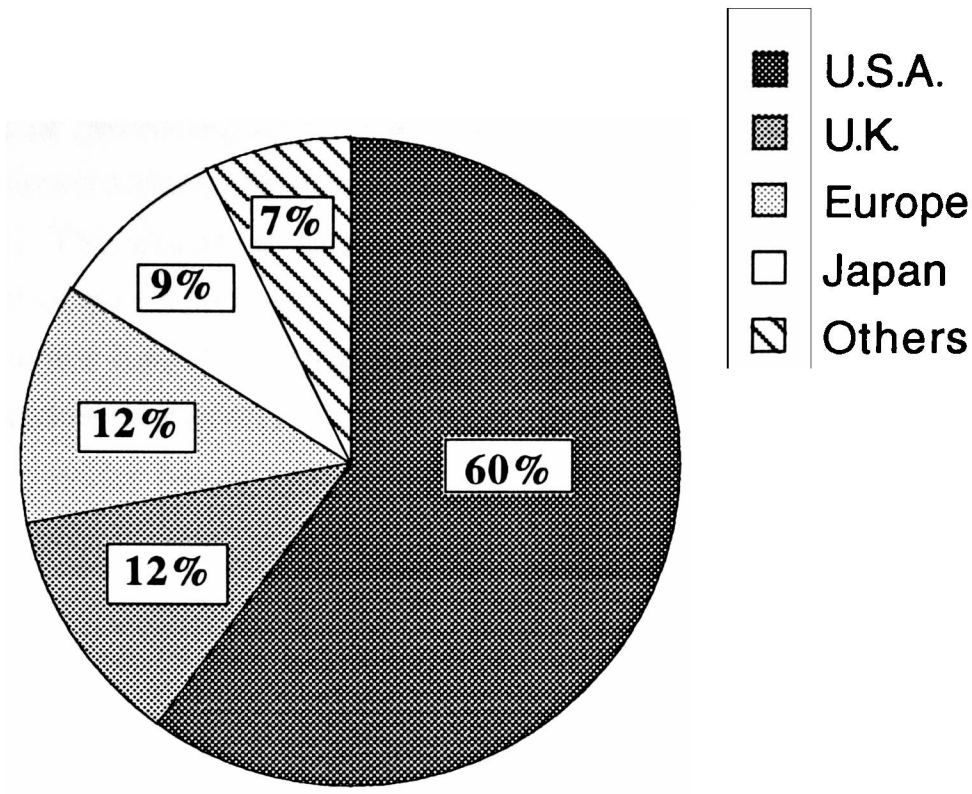


Figure 3: Investment casting world market data 1988[7]
(excluding Eastern Bloc countries)

Since the technique produces monolithic components (with no weak joints) in a range of controlled grain sizes, investment casting is being extended to produce large turbine blades, cog wheels and nuclear reactor parts. Limited creep, dimensional stability and reproducibility are key requirements for all these applications. Investment cast components display all of these properties, and the process is therefore being adopted as the preferred manufacturing route.

The product output of Deritend Precision Castings is almost entirely for high integrity markets. Castings over 250kg finished weight are being produced in stainless and low alloy steels to stringent dimensional specifications. Unfortunately, production of the larger moulds using conventional silica bonded ceramics has resulted in unacceptable failure rates of up to 40% for the company. Failure has been attributed to two main causes; casting bulge and metal-mould interaction. Casting bulge involves large areas of external casting surface being convex instead of flat and is thought to result from mould wall movement after the pouring of the metal but prior to metal solidification. Metal-mould interaction is a reaction between the metal and the mould wall producing a rough casting surface containing inclusions of refractory materials.

The initial aim of the project is to clarify the mechanisms of failure and relate them to the structure and composition of the mould. This will lead to a clearer understanding of the basic weaknesses within the structure and allow improvements to be made. The long term aim of the project is to develop a mould system capable of producing large investment castings at low failure rates. Lowering of failure rates could reduce considerable losses incurred by the foundry when castings fail to meet requirements (Table 1). This could be achieved by improvements to the existing silica binder system or by the development of a new system, ideally using sol based binders. Any alternative system will probably need to be water based as legislation introduced in 1992 to protect the environment will reduce the level of alcohol emissions allowed into the atmosphere. Almost all British foundries are looking to convert to a water based system in order to meet the requirements of the Environmental Protection Act.

CASTING	WEIGHT (KG)	MOULD COST (UNITS)	WAX COST (UNITS)	METAL COST (UNITS)	FOUNDRY COST (UNITS)	TOTAL FOR 100 CASTINGS (UNITS)	AVERAGE SCRAP RATE (%)	TOTAL LOSS FOR 100 CASTINGS (UNITS)
1	2.74	5	2.25	2.4	2.45	1210	7.4	90
2	2.41	4	3.9	21.5	5.34	3474	7.5	261
3	12.4	28.63	20.15	155.58	62.75	26,709	25	6,677
4	70.7	175	105	156.5	180.25	61,675	20	12,335
5	83.60	101	37.28	45.23	108.15	29,175	10	2,918

Table 1: Projected losses for several components currently in production at Deritend Precision Castings (Note that the values are given in unspecified units to protect the confidentiality of the foundry)

CHAPTER TWO

2.1: The Process of Investment Casting

2.1.1: Pattern Materials

Investment casting differs from all other casting processes in the use of a disposable pattern to form the cavity into which the metal is poured. The complexity, detail and surface finish of the casting is directly dependent upon the integrity and dimensional stability of the original pattern. As such, the choice of pattern material is an important step in the process of investment casting. Irrespective of the material selected, the same basic properties are required[2,5]:

1. Low ash content
2. Good fluidity to reproduce detail
3. Low contraction and expansion characteristics
4. Stable and reproducible
5. Compatibility with process materials
6. Adequate strength and hardness
7. Easy to join and assemble
8. Non toxic
9. Low cost and readily available
10. Reusable

Various tests for determining the suitability of the material have been determined and documented. Most of the test procedures are based upon those used for bitumous materials. Probably the most widely used is that of ash content but others such as softening point, thermal expansion and viscosity are equally meaningful. Many materials such as wood or mercury have been tried and tested over the last century but at present the one usually chosen for pattern production is wax or a blend of wax, resin and filler material. Ash-free medium and high impact polystyrenes are widely used to produce patterns for solid mould applications and for the production of extremely thin or fragile shaped components. Attempts to replace wax by urea or plastic have only been successful in a few specialised fields.

Wax has been used as a pattern material since the time of the early Egyptian and Chinese craftsmen. A wide range of natural and synthetic waxes have been developed to meet the exacting requirements of the industry. A choice of straight, emulsified and filled pattern wax is available to suit individual component requirements. Feeders and risers are usually manufactured from lower grade or even reclaimed wax, as the requirements for this application are less exacting.

2.1.2 Refractories

Industrial investment casting has been a growing technique for over 50 years. During this time, the refractories in use have changed very little, though geographic and economic factors have given rise to the use of a wider range of refractories[9]. Each investment foundry utilises different mixtures of refractory materials but generally the same types of material are used throughout the industry.

The first investment casting foundry to produce engineering castings did so using the 'block mould process'(Section 2.2.1). This process was characterised by a sodium silicate bonded primary investment or pre-coat, backed up by an ethyl-silicate bonded secondary investment[10]. The refractories used were sillimanite, with zircon powder or silica powder for the pre-coat. Sometimes other refractories such as cheap disposable fireclay grog or chamotte were used[4,11], but generally types of silica flour or sand (alpha quartz) were the main materials.[12,11].

When the first ceramic shell moulding technique emerged, silica continued to be the preferred refractory material. However, as new alloys were developed and new shell techniques were devised to produce larger and thinner castings, it became clear that silica was becoming more and more unsuitable. Alpha quartz, for example, is highly susceptible at elevated temperatures to small amounts of mineralisers such as metallic salts, alkali metal oxides, hydroxides and alkali-earth metal oxides which can promote fusion to form a silicate glass or even preferential crystallisation to a different structure such as tridymite or cristobalite (see Section 2.5.7). Silica also reacts with many materials at high temperatures, even in the solid state, thereby forming other compounds which influence the casting results[12].

The industry began to use successfully other readily available refractories (Table 2). These materials were highly refractory in relation to the metals being cast, but refractoriness is only one of the desirable properties for investment casting moulds. The refractoriness of a material is the ability of the substance to withstand high temperatures without fusion or decomposition.

Although the cost of the raw material is an important consideration, other relevant factors to be taken into account are:-

1) strength and mould properties,
2) casting surface finish,
3) consistent casting results,
4) ease of shell removal,
5) thermal expansion characteristics.

Table 2: Refractories in common use for investment casting in 1969[4]

REFRACTORY	COMPOSITION
Silica	SiO_2
Alumina	Al_2O_3
Chromic Oxide	Cr_2O_3
Magnesia	MgO
Zircon	$ZrSiO_4$
Zirconia	ZrO_2
Calcined china clay	42-44% alumina
Sillimanite	$Al_2O_3 . 2SiO_2$ 60-65% alumina
Mullite	$3Al_2O_3 . 2SiO_2$ 56-79% alumina
Fireclay grog	$Al_2O_3 . SiO_2$ Alumina : 40 - 80% Silica : 10 -40%

The thermal expansion of a refractory is very important as this can influence mould dimensional stability and thermal shock resistance (Figure 4). Crystalline silica has very undesirable thermal expansion characteristics due to the fact that it exists in a number of distinct allotropic forms (see Section 2.3.2). During heating or cooling, transformations between these crystalline forms (involving changes in structure or polymorphism) take place. These changes involve expansion or contraction due to molecular rearrangements. Figure 5 illustrates the variation in the coefficient of thermal expansion between quartz and cristobalite[13]. The α - β inversions (quartz at 573°C and cristobalite at 240°C) show a marked volume expansion, indeed the α - β cristobalite inversion is accompanied by a 1.5% volume change. Crystalline silica also has the disadvantage of being a health hazard when finely divided[4].

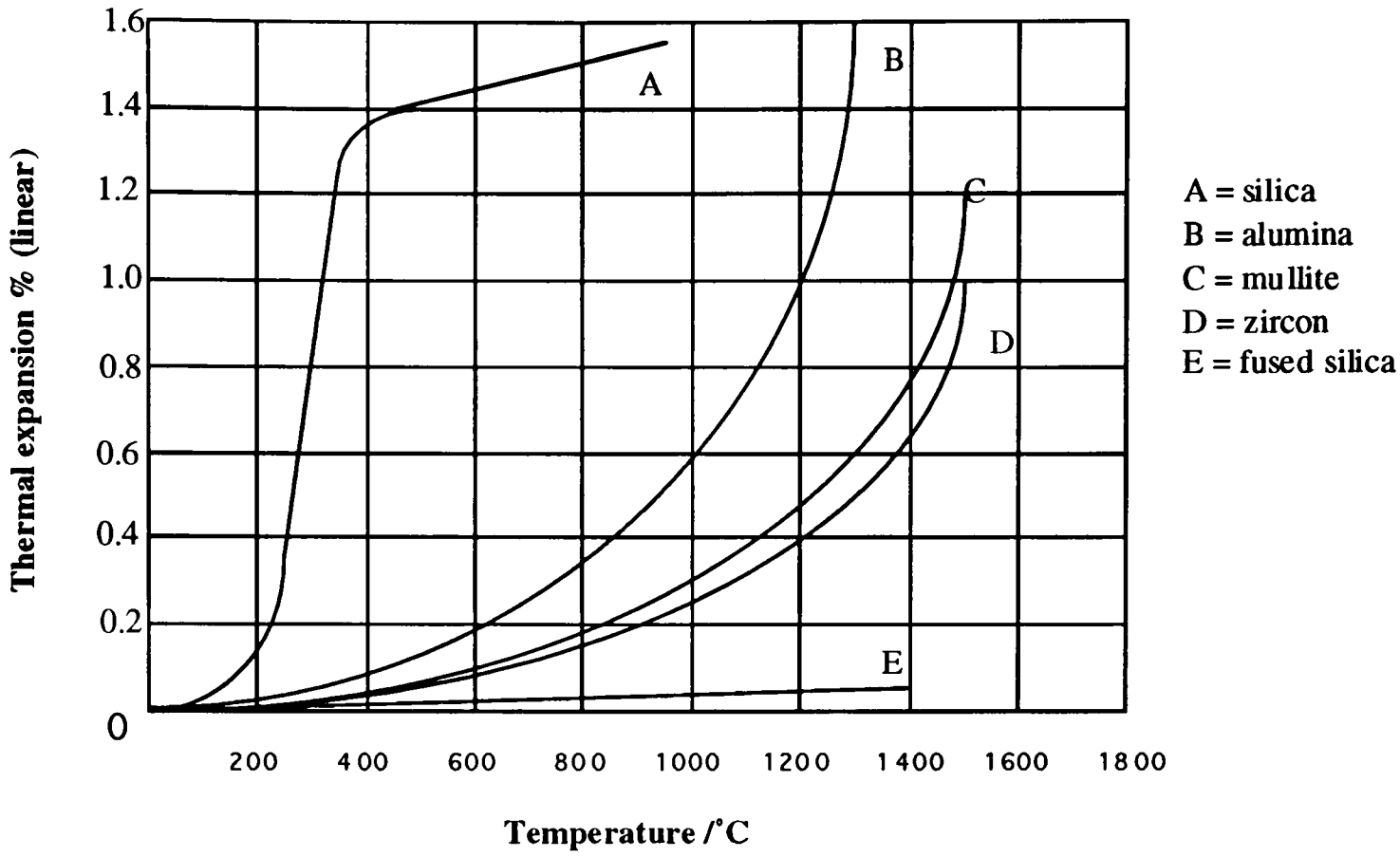


Figure 5: Thermal expansion characteristics of several refractories commonly used in investment casting[4]

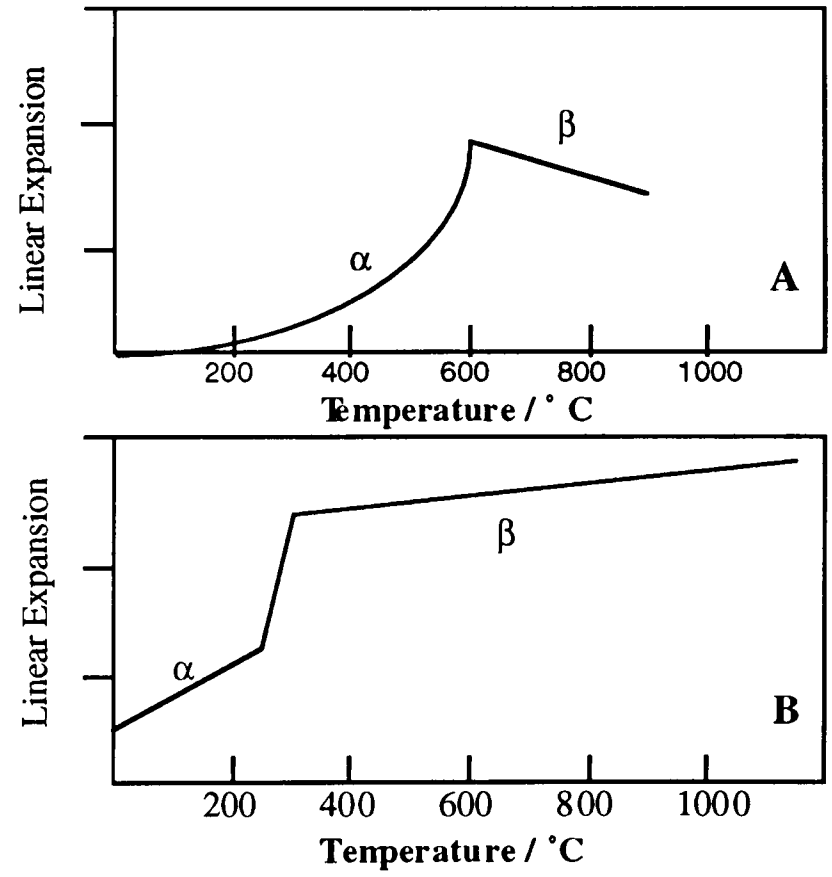


Figure 5: The thermal expasion characteristics of **A:** Quartz and **B:** Cristobalite[13]

The use of crystalline silica began to diminish, the industry preferring to use fused silica which has much greater dimensional stability. Fused (vitreous) silica is formed by heating quartz, cristobalite or tridymite above 1710°C (the fusion point) and then cooling rapidly[13]. The individual silica tetrahedra are prevented from arranging themselves in a definite order and they link in a random fashion to form an amorphous glass. A comparison between the linear thermal expansion of cristobalite and fused silica is shown in Figure 4. Since there are no structural phase changes and low linear thermal expansion due to the amorphous structure, fused silica has a very low thermal expansion coefficient of 0.56 x 10^{-6} K^{-1} (0.05% between 20 and 1000°C) and hence greater thermal stability than the crystalline forms. An illustration of the major trends in the types of refractories that have been used is shown in Figure 6.

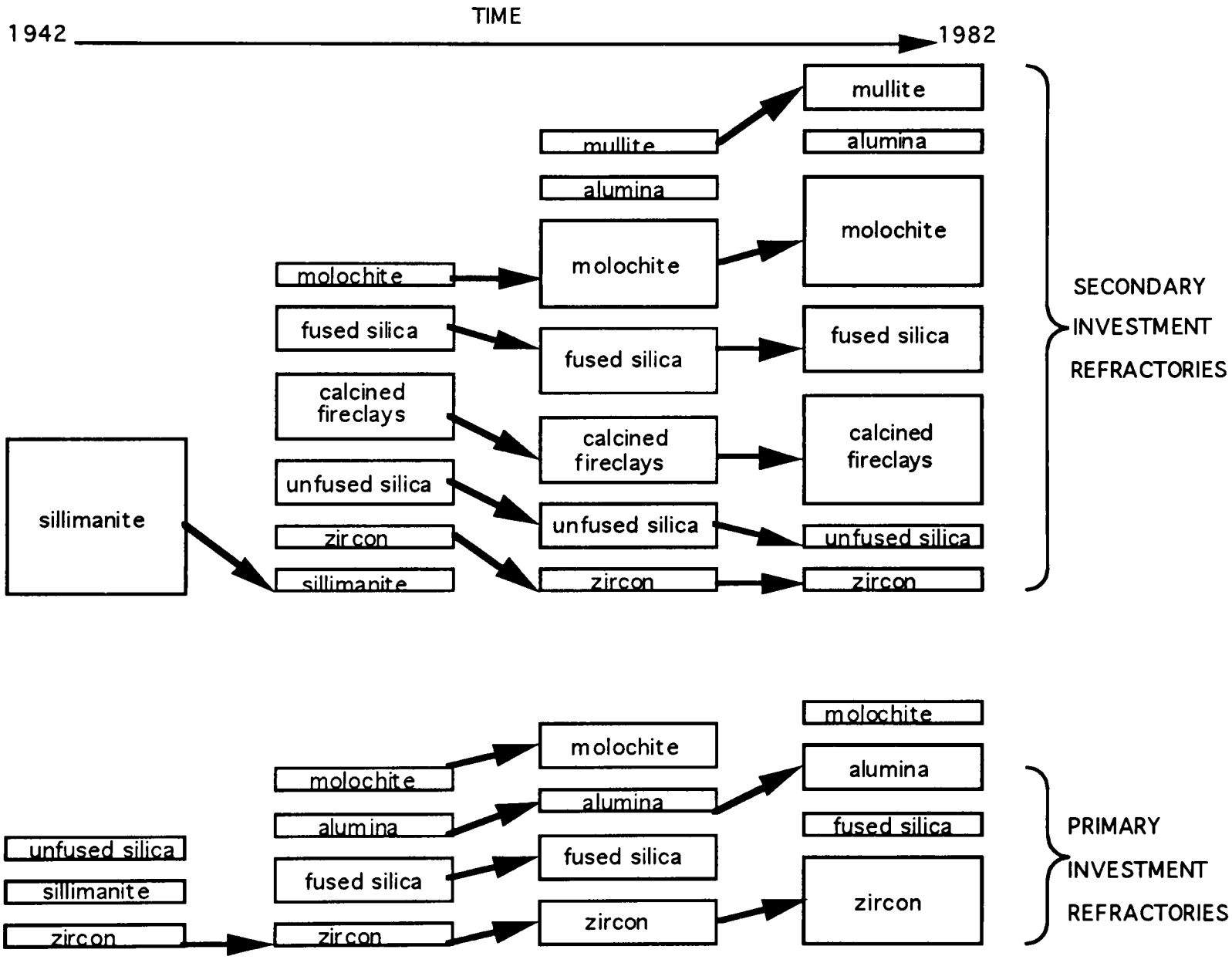


Figure 6: Major trends in the type of refractories that have been used in the investment casting industry[10]

No one single refractory has all the desired characteristics for producing an investment casting, but experience gained from using a variety of materials has led to the wide acceptance of mullite, zircon and alumina based refractories. Table 3 shows most of the refractories now available to the American and European markets while Table 4 shows the physical properties of the main refractory materials.

Table 3: Typical analysis of refractories available to the American and British markets[10]

REFRACTORIES	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	ZrO_2	BaO
Electro Fused Silica	0.15	99.7	0.015	0.02	0.015	0.023	0.002	0.007			
Unfused Silica	0.25	99.4		0.035							
Molochite UK	43.0	52.5	0.08	1.0	0.1	0.1	1.8	0.1	-		
Remasil 48 USA	47.8	49.3	1.78	0.98	0.03	0.04	0.03	0.04			
Remasil 60 USA	60.5	35.8	2.25	1.31	0.04	0.05	0.02	0.03			
Chamotte France	41.8	53.0	2.55	2.07	0.15	0.27	0.04	0.10	-		
Ceremetal France	41.0	54.0	1.6	1.6	0.2	0.2	0.2	0.2			-
Mullite Germany	75.2	24.5	0.01	0.05	0.04	0.03	0.01	0.16	-	-	-
Mullite UK	75.9	23.92	0.02	0.11	0.08	0.06	0.02	0.40	-	-	
Mullite Belgium	78.16	20.63		0.47	0.05	0.05	0.47	0.18			
Fused Alumina UK	99.6	0.01	0.01	0.01	0.03	0.02	0.01	0.19	-		
Zircon UK	0.6 max	35	0.3 max	0.2 max						64	
Zircon USA	0.28	32.6	0.22	0.06	0.02	0.02	0.01	0.01	-	63.3	-

Table 4: Physical properties of various refractories

CERAMIC PROPERTY	α MULLITE	α QUARTZ	ZIRCON $ZrSiO_4$	FUSED SILICA	ALUMINA (>99%)
Density Mgm^{-3}	2.7	2.65	3.5-4.5	2.20	3.65-3.93
Mean Linear Thermal Expansion ($\times 10^{-6}$) 25-1500°C	5.26	transforms to β quartz at 573°C over range 600 to 1000 °C $\alpha = 0$	11 - 12	0.50	9.0
Thermal conductivity $Wm^{-1}k^{-1}$	6.0668	// c axis 10.376 ⊥ c axis 4.8032	4.2258	1.6987	28.953
Melting Point °C	1850	1710 but inversions at 573, 867 and 1470°C	1538-1677	softening point approx 1600	2015

Mullite has a slightly higher refractoriness than silica and when there is an excess of alumina present the refractoriness is increased still further. Various refractory fireclay grogs have been utilised for pre-coats, for example, Molochite* and Remasil* are widely used. Unfortunately the refractoriness of alumino-silicate based ceramics is lowered by high temperatures and the presence of free silica, so the use of mullite has been restricted to secondary coats and stucco materials.

In general, alumina and zircon are the most widely used mould materials, at least as regards pre-coats. Alumina has a very high refractoriness; it is resistant to decomposition by all of the alloys normally melted and can be obtained in a very pure form. The range of alloys which can be investment cast is wider than that which can be used in any other single manufacturing process. However, the cost of a pure grade of alumina is very high, and so, for lower mould costs, zircon is used [12].

Zircon has good refractory properties, and a low thermal expansion; it is relatively non-reactive (Table 4) and is available in a range of particle sizes, which are suitable for pre-coat, secondary and stucco use. Zircon is susceptible to decomposition by sodium carbonate, sodium flouride, molten

* Refractory Trade Names

barium chloride, and all substances which are strongly alkaline at high temperature, such as Na_2O, K_2O, CaO and MgO; but the cost is reasonable and the high temperature properties are well suited to investment casting.

From 1990 to 1992, the price of high purity (low-iron) zircon refractory material increased from a few hundred pounds to over £1000 per tonne[15]. This was due to a world shortage caused by a general increase in demand and by environmental pressures limiting the quantities being mined. This increase in raw material costs motivated the investment casting industry to seek an alternative refractory material. Tests were carried out on a variety of alternatives including fused alumina, tabular alumina, Investagrog (alumino-silicate) and a series of alumino-silicate refractories called Remasil (higher alumina content). However, since the end of 1992, the price of zircon has drastically decreased making it the most widely used refractory filler.

2.1.3: Binder Systems

The binder in an investment casting mould is the adhesive liquid refractory phase which is used to form a ceramic bond between the refractory particles. The type of binder used is determined by many factors such as: size of the casting, mould firing and pre-heat temperatures, method of mould formation and the nature of the metal being cast. Alcohol based ethyl silicates and water based silica sols are the predominant binders used, but there are others such as phosphates and sodium silicates. A comprehensive list of the available binders is given below.

a) Ethyl silicate - these binders are prepared by the direct reaction between silicon tetrachloride and an alcohol:

$$SiCl_4 + 4C_2H_5OH \longrightarrow Si(C_2H_5O)_4 + 4HCl \qquad \textbf{Equation 1}$$

C_2H_5OH = ethanol

Water present in the alcohol causes some hydrolysis and polymerisation reactions to occur; so the technical grade ethyl silicate preferred for use in foundry technology is a mixture of orthosilicates (tetraethoxysilanes) and polysilicates (ethoxypolysiloxanes)[16]. The hydrolysed binder is fairly stable in the pH range 1.7 to 2.2 and least stable at pH 5[2]. A coherent gel structure is formed when an acid or base catalyst (such as ammonia) is added to the mixture of silicates. The catalyst promotes a series of polycondensation, hydrolysis and alcohydrolysis (the reverse of hydrolysis) reactions, which cause crosslinking at each silicon atom[17]. As the polymerisation sequence proceeds, the crosslinking becomes extensive causing the formation of three-dimensional polymers and, ultimately, the gel structure. The alcohol solvent is contained within the pores of the gel. This structure is dried to remove the solvent and fired at high temperatures to produce strong silica bonds.

b) Silica sols (colloidal silica solutions) - consist of silica particles (4-100 nm in diameter) normally in an alkaline aqueous solution. The silica content can be as high as 50% (by weight) although 30% solutions are more usual. The sol is converted to a gel by adjusting the pH from alkaline to acidic, by the introduction of positively charged ions or by air-drying until the sol is of a high enough concentration for the individual silica particles to collide and bond together[18]. Whichever method is adopted the gel produced is the same and provides the green bond for the mould. The high temperature bond is developed by heating the gel:

$$\text{Gel} \xrightarrow[\text{dehydrate}]{\text{heat}} \text{finely divided silica } \textit{(high temperature bond)} \qquad \textbf{Equation 2}$$

A full description of the structure, gellation behaviour and use of silica sols is given in Section 2.5.

c) Hybrid binders - often called 'prehydrolysed' ethyl silicates, and consist of a combination of ethyl silicate, colloidal silica, alcohol and other organic solvents [19]. These binders were developed to reduce the problems of rapid evaporation and short storage times that are encountered with standard ethyl silicates. Since the binders are a mixture of sol and ethyl silicate, gellation is achieved by a combination of air-drying (to gel the sol) and the use of a catalyst (to gel the ethyl silicate). Thus, both constituents are present in the final gel structure. Often a base catalyst such as ammonia is used, which gels both the sol and the ethyl silicate constituents together.

d) Sodium silicate (and potassium silicate) - sodium silicate is made by dissolving a fused mixture of silica sand and sodium carbonate in water. These silicates are rarely used in industrial applications. The sodium oxide to silica ratio varies but is usually high for investment casting applications. Unlike ethyl silicate or silica sols, sodium silicate does not form a gel; rather the bond is formed by the gradual formation of a vitreous or glassy structure by dehydration[4]. The final gel is an amorphous glassy bond assisted by a precipitate of finely divided silica[2].

e) Phosphate binders - a number of metal phosphates have been used but the most successful is magnesium phosphate[4]. Moulds bonded with phosphates are prepared by dry mixing the refractory, magnesia and ammonium phosphate and then reacting with water to form the bond (magnesium ammonium phosphate).

f) Refractory cements - the word cement is classified as 'hydraulically setting binders of the Portland cement type' i.e. calcium-alumino-silicates and calcium aluminates. Calcium mono-aluminate is produced by heating calcium carbonate with aluminium hydroxide:

$$CaCO_3 + 2Al(OH)_3 \xrightarrow[1{,}000 \text{ to } 1{,}100^\circ C]{} CaO.Al_2O_3 + CO_2 + 3H_2O \qquad \textbf{Equation 3}$$

Cement gives a good, stable, high temperature bond which is reasonably refractory but the presence of calcium has a detrimental effect on the refractoriness and so this binder is used at lower casting temperatures.

g) Plaster of Paris - is derived from the mineral gypsum (calcium sulphate dihydrate $CaSO_4.2H_2O$). After suitable calcining, gypsum loses some of the water of crystallisation to give plaster of Paris ($CaSO_4.O.5H_2O$). When mixed with water the plaster rehydrates and goes into solution. This solution becomes supersaturated and $CaSO_4.2H_2O$ crystallises, forming a bond by mechanical interlocking of the crystals[4].

$$2CaSO_4.0.5H_2O + 3H_2O \longrightarrow 2CaSO_4.2H_2O \text{ (crystals)} \qquad \textbf{Equation 4}$$

The bond is reasonably stable at lower temperatures but above 750°C dissociation to calcium oxide and sulphur dioxide takes place.

2.1.4: Binders Being Developed

The binder used to build a ceramic shell plays an important role in the quality of the casting produced. For many years colloidal silica, ethyl silicate and hybrid ethyl silicate binders have been used successfully to produce good quality investment castings. However, recent developments such as the casting of reactive alloys, directional solidification techniques and the introduction of larger castings have highlighted several deficiencies in the high temperature performance of silica binders. These include extensive reaction of the silica binder with the metal being cast to form silicate inclusions in the surface of the component, high temperature creep (possibly leading to mould buckling), and the occurence of phase changes which have detrimental effects upon the thermal and mechanical stability of the moulds. Subsequently, a great deal of research has been carried out to improve or replace silica as a binder.

a) Silica Binders - the use of ethyl silicate and hybrid binders is becoming more restricted as new regulations come into force concerning the environmental hazards produced by organic solvents. Water based silica binders are therefore being developed as a replacement.

Two such proprietary binders being developed are Primcote[20] and Fascote[21]. Primcote and Fascote are primary and secondary coat binders, respectively, both of which contain colour indicators which turn from green to yellow when the shell is dry. This system is reported to eliminate buckling, lifting and cracking of the individual coats[20] to produce a mould with much higher green and fired strengths than conventional silica bonded moulds. Unfortunately, the available references are commercially orientated and no explanations for the reported improvements are given. However,

since spalling of investment coats is usually linked to reduced solvent content it would be reasonable to assume that the presence of moisture indicators prevents each coat from being overly dried, and hence, prevents the occurence of spalling.

b) Zirconia Binders - these are being developed for applications requiring high temperature resistance (the melting point of ZrO_2 is 2,690°C and the maximum usable temperature is 2,000°C)[21]. The production of a refractory body using colloidal zirconia improves the resistance to deformation at high temperatures.

Two zirconia binders currently being produced are Remet zirconia sol[22] and Zirmast[23]. Both have been used to produce refractory shapes with greater temperature resistance and less metal-mould interaction than identical silica bonded moulds. Zirconia sols are, therefore, possible substitutes for silica in the production of investment casting moulds.

c) Alumina Binders - these are non-fibrous, aqueous, acidic dispersions of alumina monohydrate (boehmite) usually stabilised with nitrate ions producing a weak solution of nitric acid[22]. The average percent alumina is 19 to 20% (by weight) although this dispersion can be diluted to any concentration with water. The binder is used in the same manner as colloidal silica but is more susceptible to gellation by reactive refractory materials.

After firing, the bond formed is Al_2O_3. Alumina has a very high melting temperature (2050°C), high refractoriness and low reactivity with alloys and so alumina bonded moulds have the potential to replace silica bonded moulds. A method of using alumina to make a ceramic mould has been patented[24] using Remal 20[22] which is a proprietary binder.

d) Mullite/Alumino-silicate Binders - mullite ($3Al_2O_3.2SiO_2$) is the only crystalline phase in the alumina/silica system that remains stable from room temperature through to elevated temperatures[25] (melting point 1823°C ± 10°C). Extensive interest is being shown in the use of mullite as a binder material due to its high refractoriness, low thermal expansion and conductivity, good chemical and thermal stability and high creep resistance[26]. Mullite can be prepared by homogeneously mixing a boehmite (alumina hydroxide) sol and a silica sol together, in the stoichiometric ratio of 3:2. This sol mixture is then gelled at pH 3 and fired at 1300°C for complete mullitization[26].

A proprietary alumino-silicate binder is available called Magna Bond B[27], containing a mixture of Al_2O_3 and SiO_2 sol particles, which, when fired, give an alumino-silicate with an alumina/silica ratio of 5/17. This alumino-silicate bond gives very high green and fired mould strengths and exhibits low reactivity with molten alloys.

e) Mixed Sol Binders - a series of zirconia/mullite[28] and zirconia/alumina[29] mixed binders have been produced in an attempt to create a ceramic bond which matches the chemistry of the refractory aggregates being used. This should make the ceramic body more stable and allow the advantageous properties of both constituents to be simultaneously exploited.

f) Aluminium Nitrate - this is an aqueous solution of aluminium nitrate or hydroxy nitrate which is heated or treated with an alkali to produce the ceramic bond[4]. The binder is being developed in Russia in an attempt to produce a silica-free mould, but very little information is available about the chemistry or the use of these binders.

2.2: Investment Techniques

2.2.1: The Block Mould Process

For certain applications, such as the casting of very small parts, it is often preferable to use an investment method known as the block or solid mould process. The technique was introduced in 1887[2] and was for many years a successful manufacturing route. Block moulds can be either single or double invested depending upon the required casting surface. Double investment moulds differ from single investment moulds only in the use of a primary coat which is applied to the wax pattern prior to the main investing cycle.

A schematic illustration of the basic principle is shown in Figure 7. The primary coating, consisting of binder and fine grained ceramic refractory, is applied to a wax pattern by spraying or dipping. Whilst the coating is still wet, coarse refractory particles are applied as a stucco and the assembly allowed to dry. The coated pattern is then inverted, fastened to a mould base plate and placed into a suitable metal flask. The flask is then filled with a slurry made from refractory and liquid binder. The assembly is vibrated to consolidate the investment and to obtain an intimate contact between pattern and slurry. The investment is then gelled, either by the prior addition of accelerators, or by gentle heating at temperatures below the softening point of the wax. After gellation excess binder and refractory which will have risen to the surface is removed.

The mould is then transferred to a low temperature oven for several hours at a temperature of 150°C. This treatment removes the wax pattern and develops the green strength of the mould. At this point the flask is usually removed from the mould but when added support during both handling and casting is required a flask made from heat resisting steel is used and left in place. Firing of the mould at approximately 1,000°C takes place prior to casting with the metal.

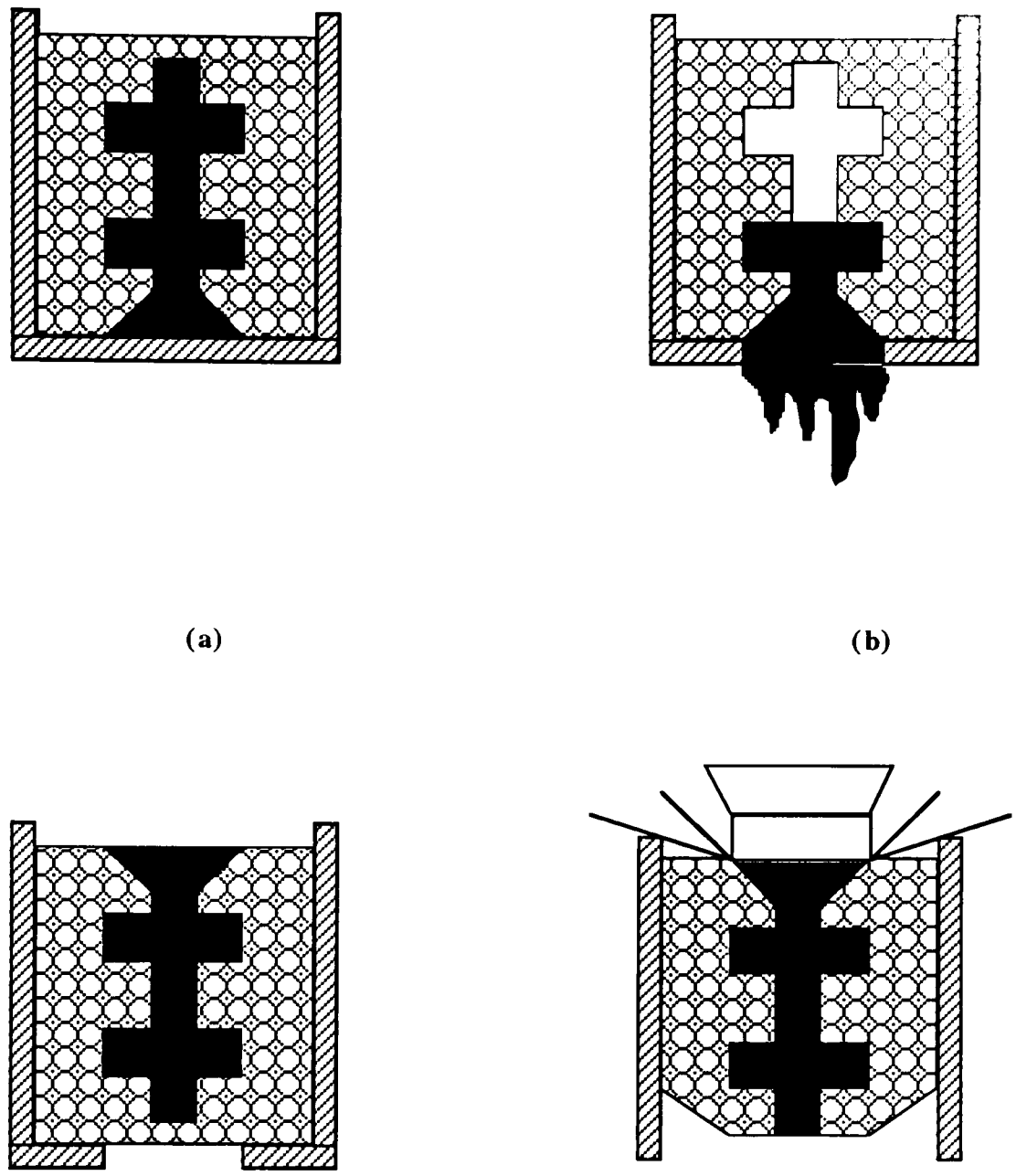


Figure 7: The block mould or solid mould process[2]

(a) A metal flask is placed around the pattern cluster and filled with investment slurry

(b) After mould material has set and dried the patterns are melted out of the mould

(c) Hot moulds are filled with metal by gravity, pressure vacuum or centrifugal force

(d) Mould material is broken away from the casting

2.2.2: The Shaw Process

Ethyl silicate slurry moulding (also known as the Shaw process, Avnet-Shaw Osburn-Shaw process and the Dean Process) is a variation of the investment technique which originated in the UK[30]. The principal difference between this process and other investment methods is that a gelling agent is added to the refractory slurry before it is poured over the pattern. When this mixture forms a flexible gell, the mould can be stripped off the pattern and fired to develop full ceramic strength.

The basic principles of the process are summarised in Figure 8. Patterns can be made of various materials such as plaster, wood or metal and can be reused which is not possible when using an expendable (wax or plastic) pattern. A mixture of graded refractory, hydrolysed ethyl silicate and a liquid catalst are mixed together to form a slurry. This mixture is poured over the pattern and allowed to gel. The mould is then stripped from the pattern and torched with a high pressure gas flame. This ignites any remaining alcohol within the binder and forms a series of craze cracks throughout the entire mould section. The presence of the cracks produces a mould of high permeability which is partially immune to thermal shock. Further strengthening is achieved by firing at high temperatures. The resultant mould is inert, gas-free, erosion resistant and collapsible and can be cast successfully at both high or room temperatures.

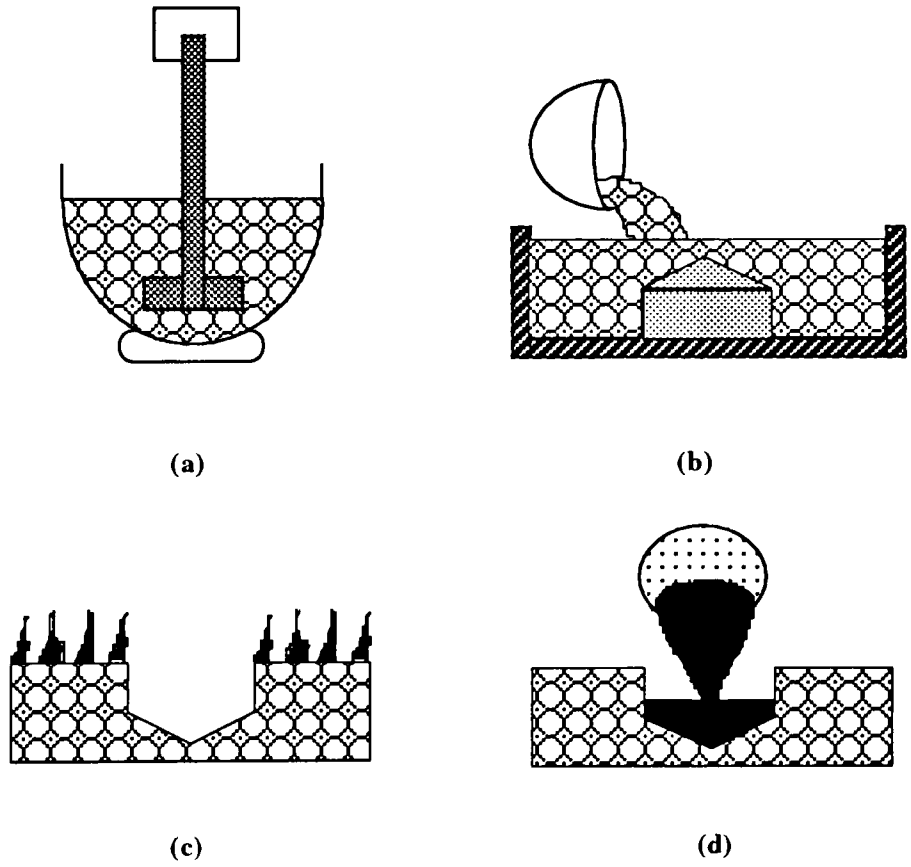


Figure 8: The Shaw Process

(a) A small percentage of gelling agent is added to the binder and mixed with the refractory
(b) The slurry is poured over the pattern and allowed to gel
(c) Mould is stripped from the pattern and ignited to form the 'microcrazed' structure
(d) The fired mould is cast with liquid metal

The process has several advantages including the use of a permanent pattern that does not need precoating, the ability to produce undercut shapes and the relative ease with which larger components can be cast. Unfortunately the master pattern is expensive and the accuracy of the pattern can be impaired by the split mould. The moulding process is slow and the casting surface is rougher than that obtained using other investment techniques[31].

2.2.3: The Mercast Process

The Mercast process can be classified as an investment technique because it involves the use of two basic characteristics: a disposable pattern and a monolithic mould. The unique feature of the process is the use of mercury as a pattern material. Mercury is poured into a suitable die and then passed into a refrigerated area where it is 'frozen' until solid[4]. The solid pattern is removed from the die and processed at sub-zero temperatures to prevent the mercury from liquefying. Ceramic shell moulds are formed around the pattern by repeated dipping in specially prepared slurries which consist of zircon-based ceramic material mixed with a liquid such as freon which has a low melting point. Where one slurry is usually used for dipping of wax, a minimum of twenty dippings in several slurries of increasing viscosity are used[9]. The particle size of the ceramics used is very fine, usually 600 mesh (27μm) or under and the slurry temperature is maintained at or near to -93°C to minimise volatilisation of the solvent. The drying time between each dip is of the order of a few seconds since each layer is only approximately 5×10^{-3} cm thick.

The mercury is melted from the mould carefully to prevent cracking of the ceramic. Firing takes place at 1,000°C for approximately two hours. Moulds can be removed from the furnace and air-cooled without cracking and likewise reheated to any temperature prior to metal casting. After casting, the mould is removed by vibration. This is a relatively simple process due to the thinness of the ceramic shell.

The use of mercury as a pattern material has several advantages. Unlike wax or plastic which have changes in volume during solidification of around 8-9%, mercury changes volume by only 3.5%. This relatively low expansion prevents damage to the weak and fragile shell during pattern removal. Mercury also possesses a high thermal conductivity which results in much faster solidification rates during pattern production. Solid mercury has similar properties to lead[32] and as such is rigid, possesses a small amount of mechanical strength and does not creep when used for this application. However, the capital expenditure for the installation of refrigeratred areas in a foundry is substantial and the mercury itself is expensive. Aside from the obvious health hazards associated with mercury, there also exist many health and safety and environmental legislation which would prevent the industrial use of both mercury and freon in present day foundries.

2.2.4: The Investment X Process

This process was developed by J. S. Turnbull at Metropolitan Vickers Electrical Company in 1955[33]. A standard wax pattern is first given a thin precoat layer of zirconia refractory by spraying or dipping. The following coats, usually around 7 to 8 in total, are applied by dipping into a slurry consisting of ethyl-silicate binder and silica refractory and stuccoing with coarse alumino-silicate particles. Each layer is allowed to set and dry thoroughly before the next is applied. The total thickness of the shell varies between 7 x 10^{-3} m and 12 x 10^{-3} m depending upon the number of layers applied and the coarseness of the stucco material.

Shells are dewaxed in a solvent-vapour bath using trichloroethylene. Wax, dissolved in trichloroethylene, drains into the bottom of a tank and is collected. By use of distillation, both solvent and wax are recoverable and reusable. Each shell is placed into a canister and surrounded by a coarse refractory medium. Some binder may be added to the back-up to strengthen the aggregate. The entire assembly is then fired at 1,000°C. Casting is done centrifugally, with the canister being rotated during pouring of the metal. If the shell contains more than one casting cavity, the cavities are symetrically arranged in a radial pattern in order to achieve equal distribution of the metal. alloys that can be cast using the process include high-temperature alloys, stainless steels, low-alloy steels and various non-ferrous alloys[34].

From a technical standpoint the process has several advantages. The mould has a high and consistent permeability which reduces the thermal capacity and allows the moulds to be cast at the lowest possible temperature. Mould cracking is eliminated with the primary coat unaffected by the solvent during dewaxing which removes the flaking that can sometimes occur in conventional dewaxing processes. Less refractory material is used which reduces mould weights and costs.

2.2.5: The Glascast Process

The Glascast process was developed by the Corning Glass Co. in 1955[34] and is similar to the Shaw process in that a match-plate of wood, plastic or metal is used. A shell is built up by a series of dip and stucco operations with controlled drying of the layers between successive dips. The main constituent of the slurry is a finely divided, highly stable form of glass with the nominal composition: 96% SiO_2, 2.5% B_2O_3 and 1.5% other constituents. This powder has a very low thermal expasion and was developed and adapted especially for the casting industry. Various binders can be used including acidified water, ethyl silicate, sodium aluminate and phosphates. The stucco may consist of various refractory materials but foamed glass was often used.

Moulds are dewaxed by the 'flash' method at 925 - 1050°C. After complete removal of the wax the moulds are left in the furnace for a short period to complete the sintering of the ceramic. After cooling the moulds can be cast cold or even reheated before casting to reduce thermal shock.

Unlike other investment techniques the Glascast process is designed to produce small components with excellent surface finish and dimensional control. By pouring into an unsupported shell the casting is rapidly solidified which leads to finer grain size, less decarburisation and less metal-mould interaction. However an unsupported shell cannot be used to cast components gretaer than 2.5 kg metal weight[35].

2.2.6: The Lost Foam Process

The lost foam process is currently being used in the production of aluminium, grey iron and ductile iron components. The technique originated around thirty years ago[36] when expanded polystyrene became commercially available. It was manufactured as large blocks which could be cut and shaped like wood to form component patterns. Foundries took advantage of this versatility to produce large one-off castings using a mould produced from hardened resin bonded sand. In 1964 the resin was removed, the process repatented[37] and the castings began to be produced using unbonded sand. In the late 1970s, several large foundry organisations including Ford, General Motors, Teksid and SCRATA began to develop the process into a practical method for producing high volume castings. At present around 100 foundries use the technique on a commercial basis[36].

The raw material for making patterns is in the form of small spherical beads of polystyrene mixed with a blowing agent such as pentane. These beads are blown into the cavity of an aluminium die which is steam heated to expand and fuse the individual beads. After cooling the pattern is ejected. Complex patterns are assembled from several pieces using glue. Individual patterns are attatched to a sprue to form a cluster which is dipped into a refractory paint to form to give a coating thickness of approximately 0.3 to 0.5 mm. The coated cluster is then placed into a steel flask and surrounded with dry silica sand which is compacted by vibration. Metal is poured down the sprue which vapourises and replaces the pattern. After cooling the casting is extracted.

The reproduction of the pattern is good, with corners, bolt holes and surface detail being reproduced exactly. There are no join lines to be ground off and the residual sand and coating are easily removed from the casting. However, there are several inherent problems which produce defects in the castings, the most obvious of which is the possibility of metal contamination by pattern material. The flow of metal into the pattern cannot be controlled and metal turbulence can be produced. There is also some concern regarding the ability to produce and precoat foam patterns without some degree of distortion or inaccuracy.

2.3: The Silica Minerals

2.3.1: Basic Silicate Structure

Silicon is one of the most abundant elements in the earth's crust, occuring mainly in combination with oxygen as silica SiO_2 and with oxygen and other elements as silicates[13]. Silica is a polymorphic substance, capable of existing in several forms, all having the same empirical formula but differing in the arrangement of the structural units. The packing of silicon and oxygen atoms in silica minerals and silicates consists of four oxygen ions arranged around a central silicon ion (Figure 9). This arrangement is characteristic of all compounds containing silicon and oxygen because the tetrahedrally coordinated structure allows charge neutrality to be maintained together with close packing of the ions to produce maximum structural stability[13].

The silica tetrahedra are linked in a close packed structure with all four corners of each tetrahedron being shared with other silica tetrahedra[38]. Even this rigid structure allows silica to exist in several different polymorphic forms corresponding to different ways of combining tetrahedral groups with all four corners shared.

2.3.2: The Polymorphic Forms of Silica

Three distinct crystalline forms are recognised; quartz, tridymite and cristobalite. In quartz the Si-O-Si bonds between neighbouring tetrahedra are bent around to form a spiral chain. Overall the structure consists of many such spiral chains, joined by common silicon ions, and forming an essentially hexagonal crystallographic structure (Figure 10(a)).

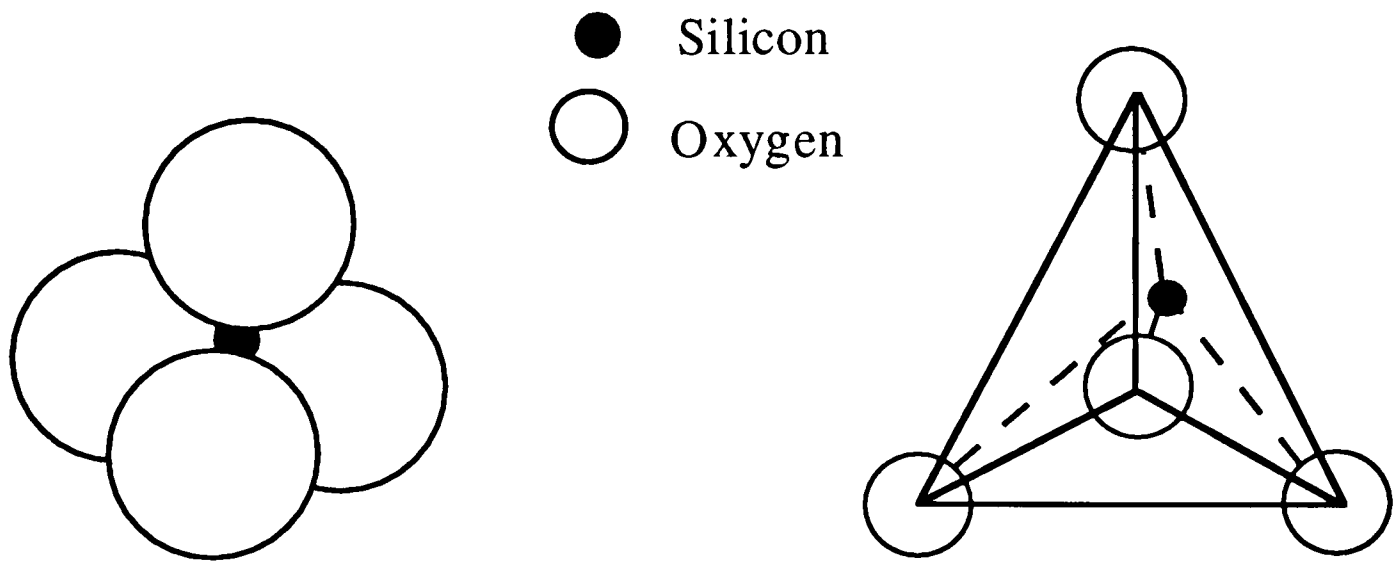


Figure 9: The basic silicate structure[13] a) Packing of silicon and oxygen atoms
b) A silicon-oxygen tetrahedra

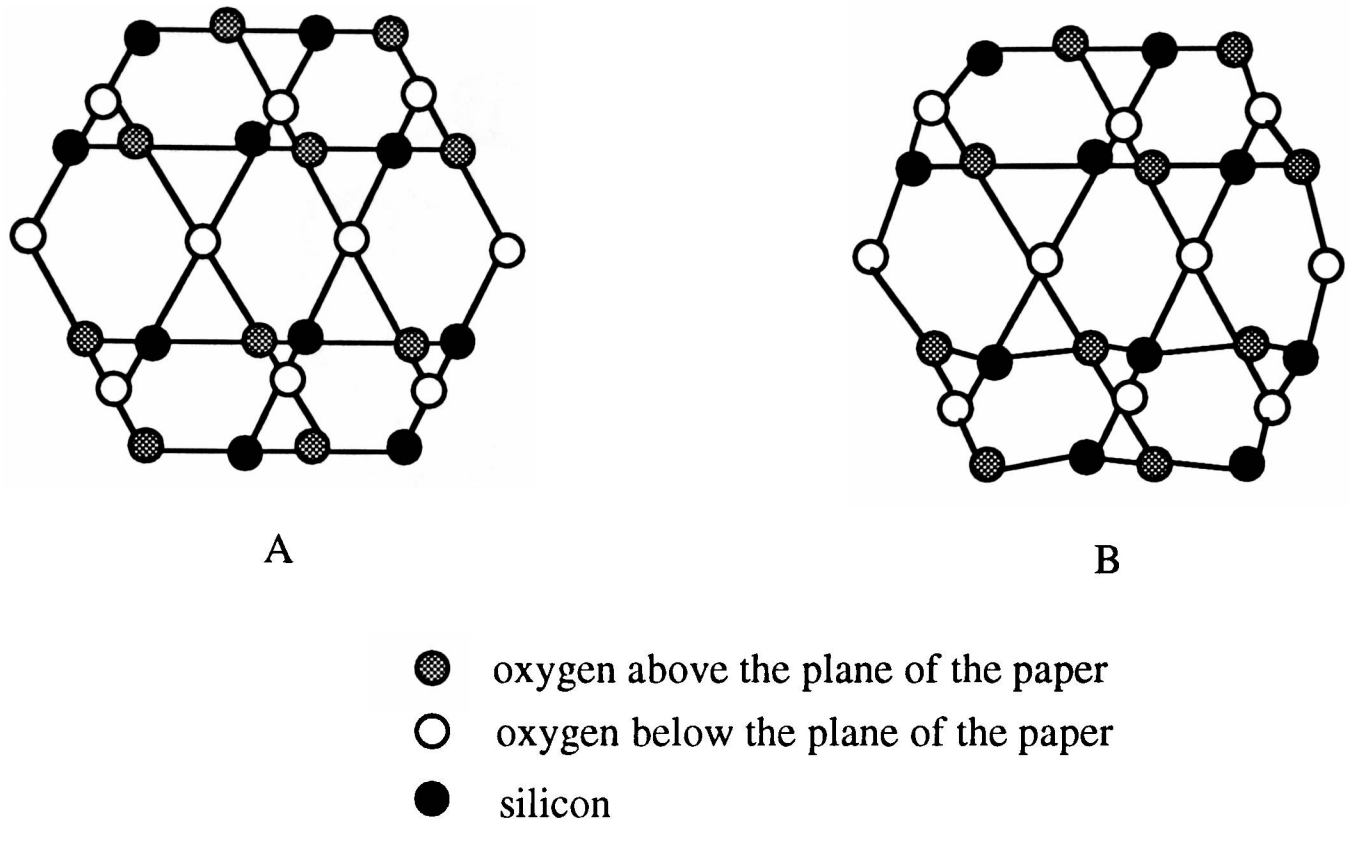
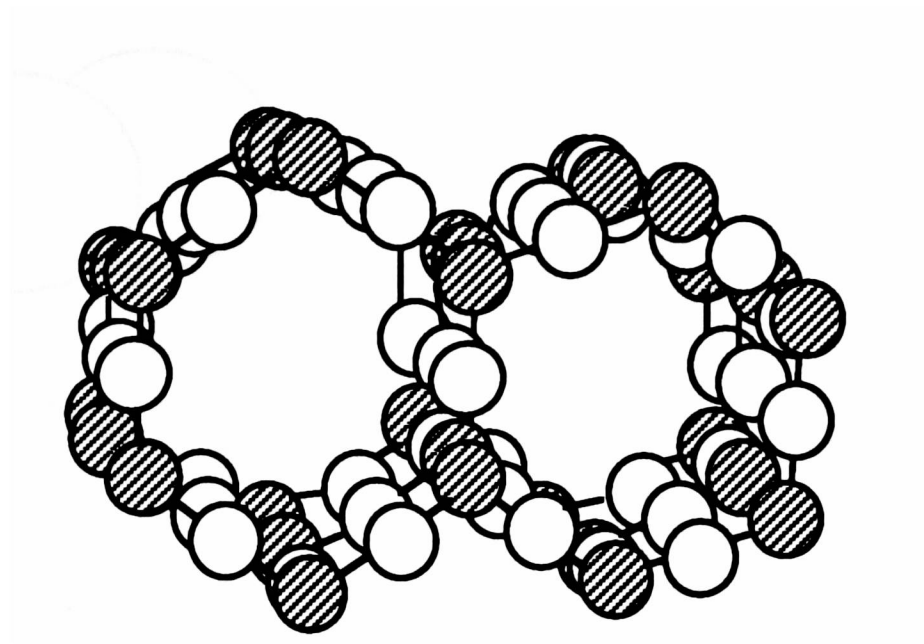
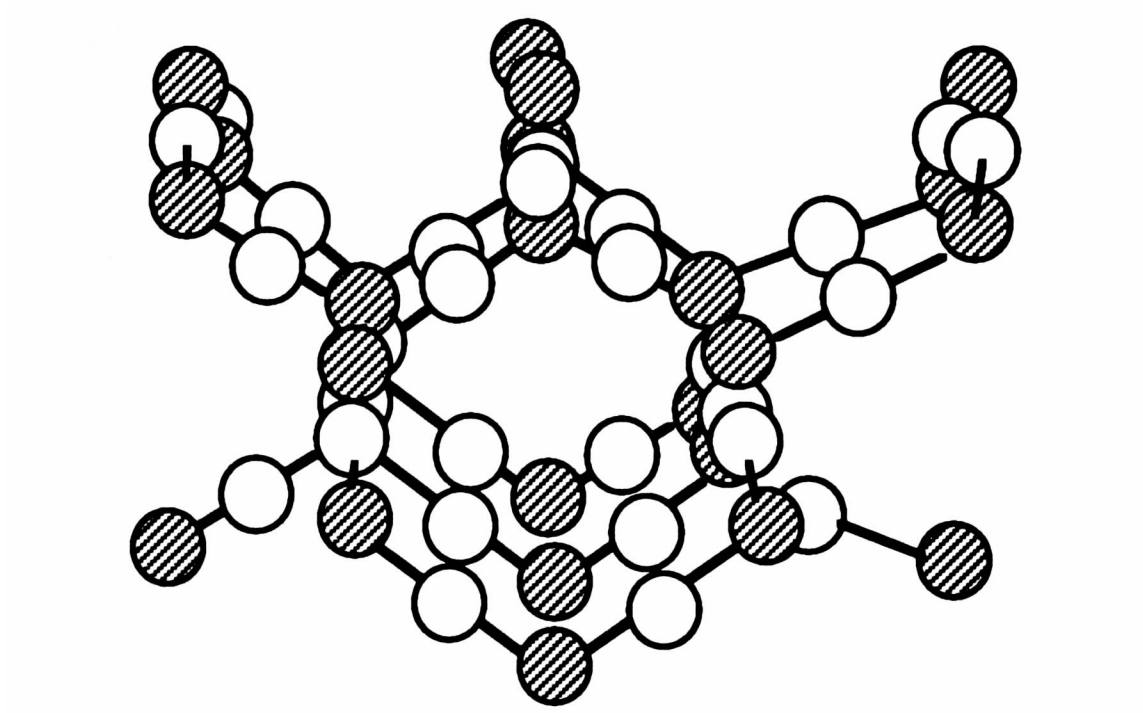


Figure 10: Arrangement of silicon atoms in: A) β quartz B) α quartz[13]

The structures of tridymite and cristobalite consist of rings containing six Si atoms and six O atoms formed by the silica tetrahedra (Figure 11). The rings are slightly distorted so that the Si atoms are not all in the same plane. Figure 12 illustates how the silica tetrahedra are linked. In tridymite (Figure 12(a)) the second layer of oxygen atoms lie directly above the first layer and the structure is essentially ABA trigonal. In cristobalite (Figure 12(b)) the second oxygen layer is slightly displaced corresponding to the two layers being twisted through 60° with respect to each other. Thus cristobalite has an essentially ABCBA cubic structure.



(a)



(b)



Figure 11: The structures of; (a) Tridymite (b) Cristobalite[13]

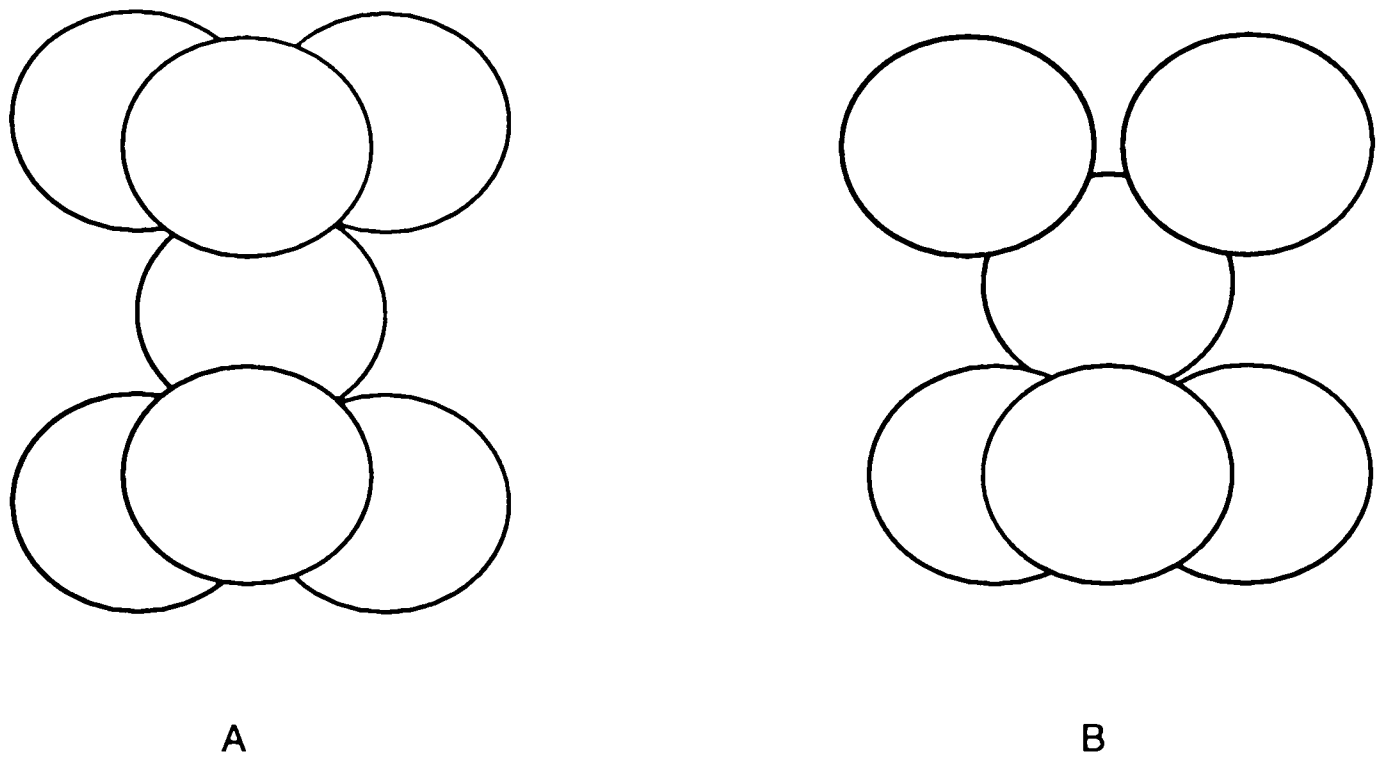


Figure 12: Packing of oxygen atoms in A. Tridymite and B. Cristobalite[13]

All three polymorphic forms are capable of existing in more than one modification with different crystal structures[38]. The transformations are temperature and pressure dependent and the temperature stability ranges of the various modifications are summarised in Figure 13 and graphically represented in Figure 14.

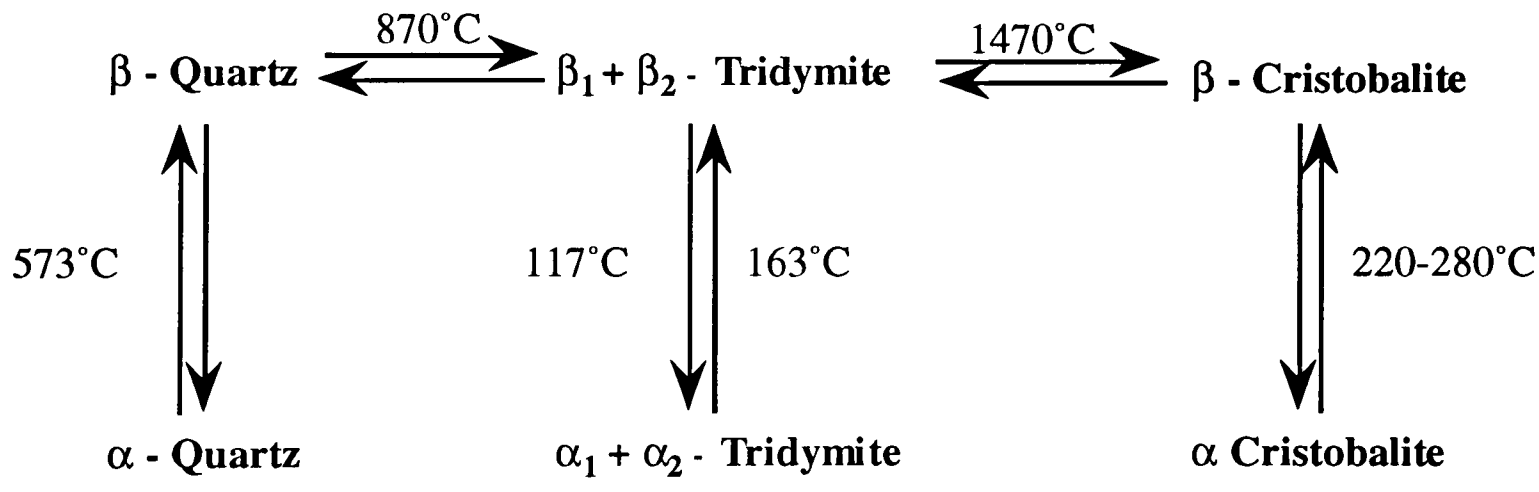


Figure 13: The temperature stability relationships in the silica system

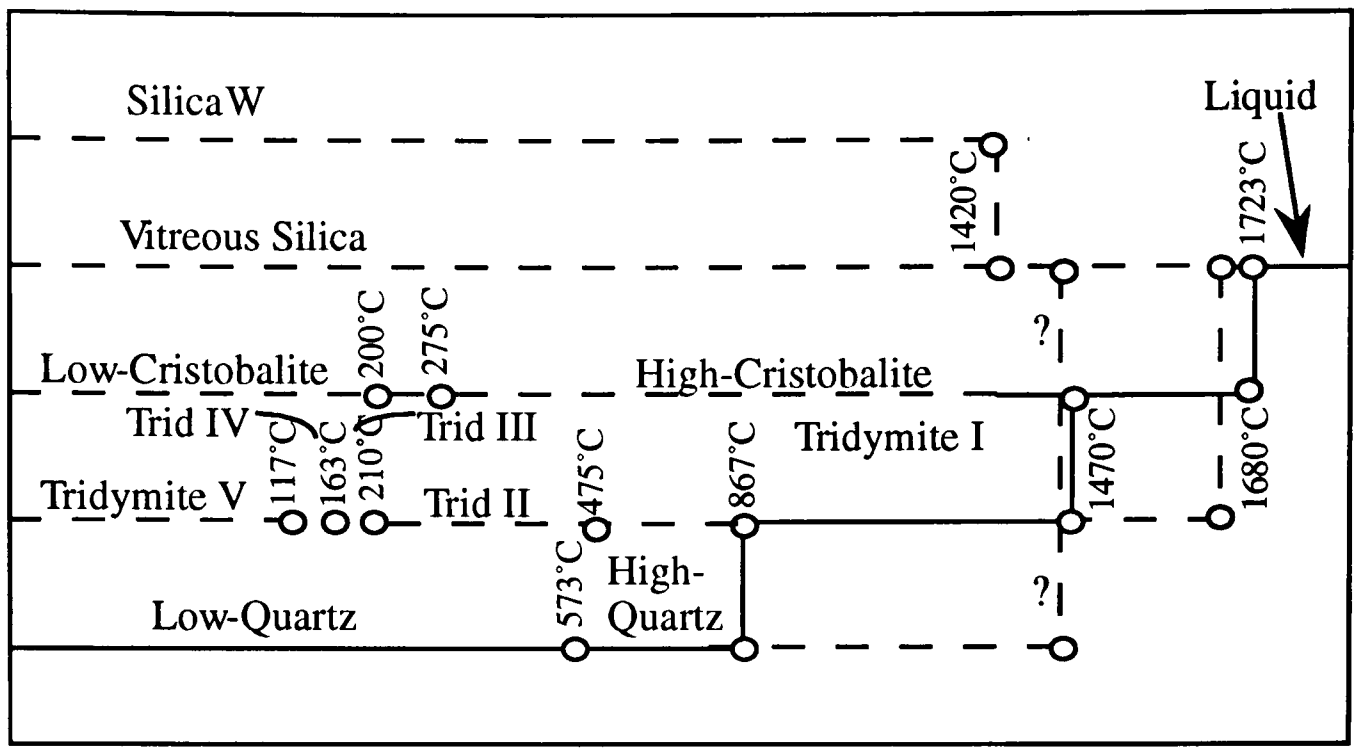


Figure 14: SiO_2 stability relations at one atmosphere pressure, as revised in 1955[39]
Ordinate is undefined measure of stability
Solid lines represent stable state, dashed lines represent metastable state

The transformations between the various forms are of two types:

a) Conversions (β forms)- where quartz changes to tridymite and then to cristobalite[38,40]. The structures of the three forms of silica differ considerably and so it is not easy to convert from one to the other. These changes involve the disruption of existing bonds and subsequent formation of new ones. the conversions can be represented by the equation;

$$\text{Quartz} \xrightarrow{1470℃} \text{Cristobalite} \underset{}{\overset{870℃}{\rightleftharpoons}} \text{Tridymite} \qquad \textbf{Equation 5}$$

Since the cristobalite and tridymite structures are similar, transformations between the two forms occur more readily than that of quartz to cristobalite. Quartz has an entirely different structure and it is not surprising that cristobalite and tridymite cannot be reconverted to quartz. Although these transformations are theoretically reversible they involve a complex rearrangement within the crystal, and thus, not surprisingly, the changes are sluggish and take place only with difficulty. This allows some of the phases to exist metastably outside the defined temperature stability ranges, for example, pure quartz can be raised to the melting point without any appreciable conversion into cristobalite or tridymite taking place. Surprisingly, quartz is the more common SiO_2 phase in Nature, with many forms such as ganister, flint and sandstone occuring naturally in large quantities. Indeed, SiO_2 is the most abundant mineral in the Earths crust. Cristobalite and tridymite are formed artificially by treatments at high temperatures.

b) Inversions- are the transitions between the α and ß varieties (low and high temperature forms, respectively) and involve only slight structural rearrangements[38]. Bond angles are altered as the structure assumes a lower order of symmetry, but unlike conversions there is no breaking of Si-O bonds or rearrangements of silica tetrahedra. The β forms, which are stable at higher temperatures, are symmetrical, whereas the α forms are the distorted versions of the β structures (see Figure 10). These inversions are instantly reversible and occur as the crystal is heated or cooled.

Silica can also exist in a non-crystalline form which has no long-range molecular lattice structure (Figure 15). The orientation of one tetrahedral group with respect to a neighbouring group about the connecting Si-O-Si bond is random[41]. The X-ray diffraction pattern shows a single broad diffraction peak corresponding to a spacing of 4.32 Å, which is equivalent to the most intensive cristobalite peak (Figure 16). Each atom thus has a definite number of nearest neighbours at a definite distance, giving rise to the observed diffraction pattern, but there is no periodicity in three dimensions and the substance is non-crystalline[42].

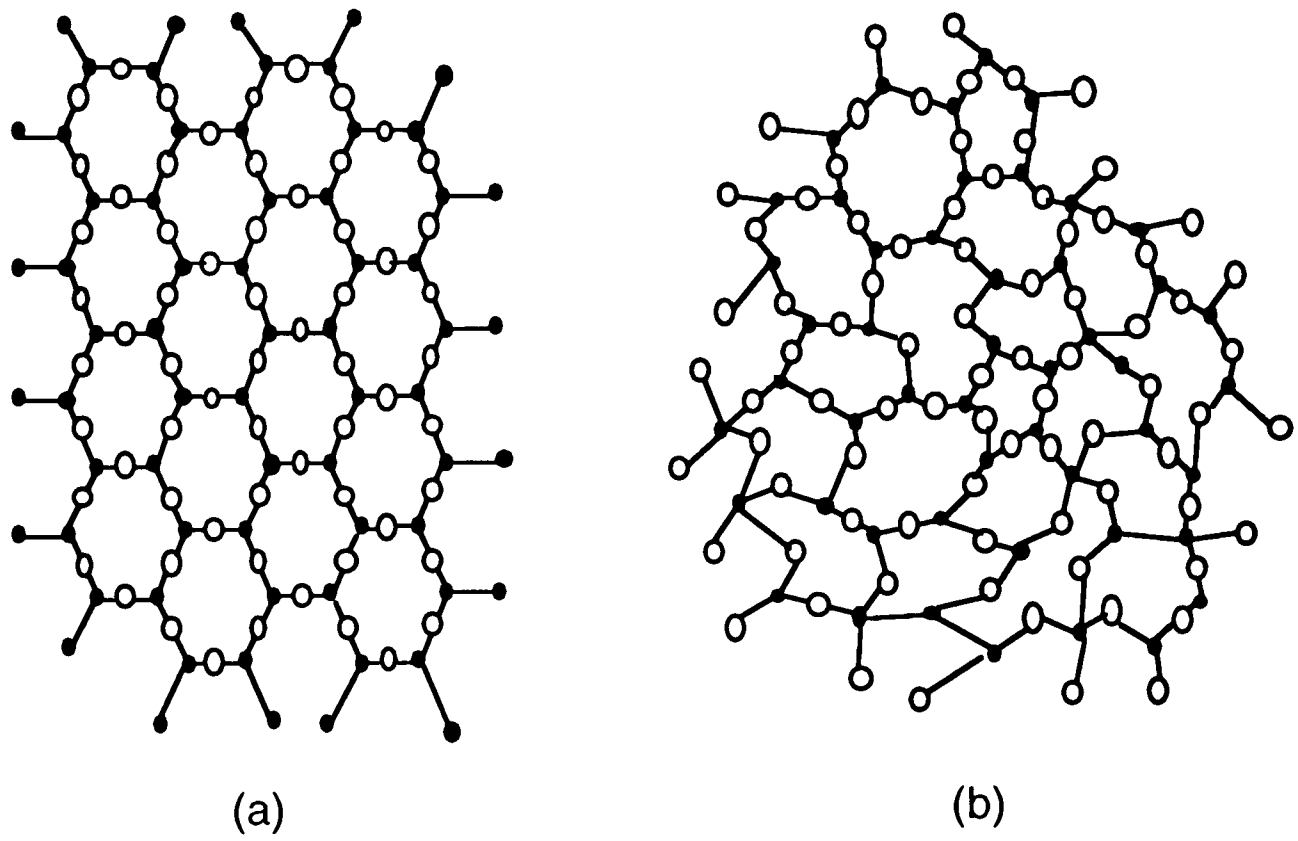


Figure 15: Schematic illustration of the molecular structure of
a) a silica mineral
b) a silica glass

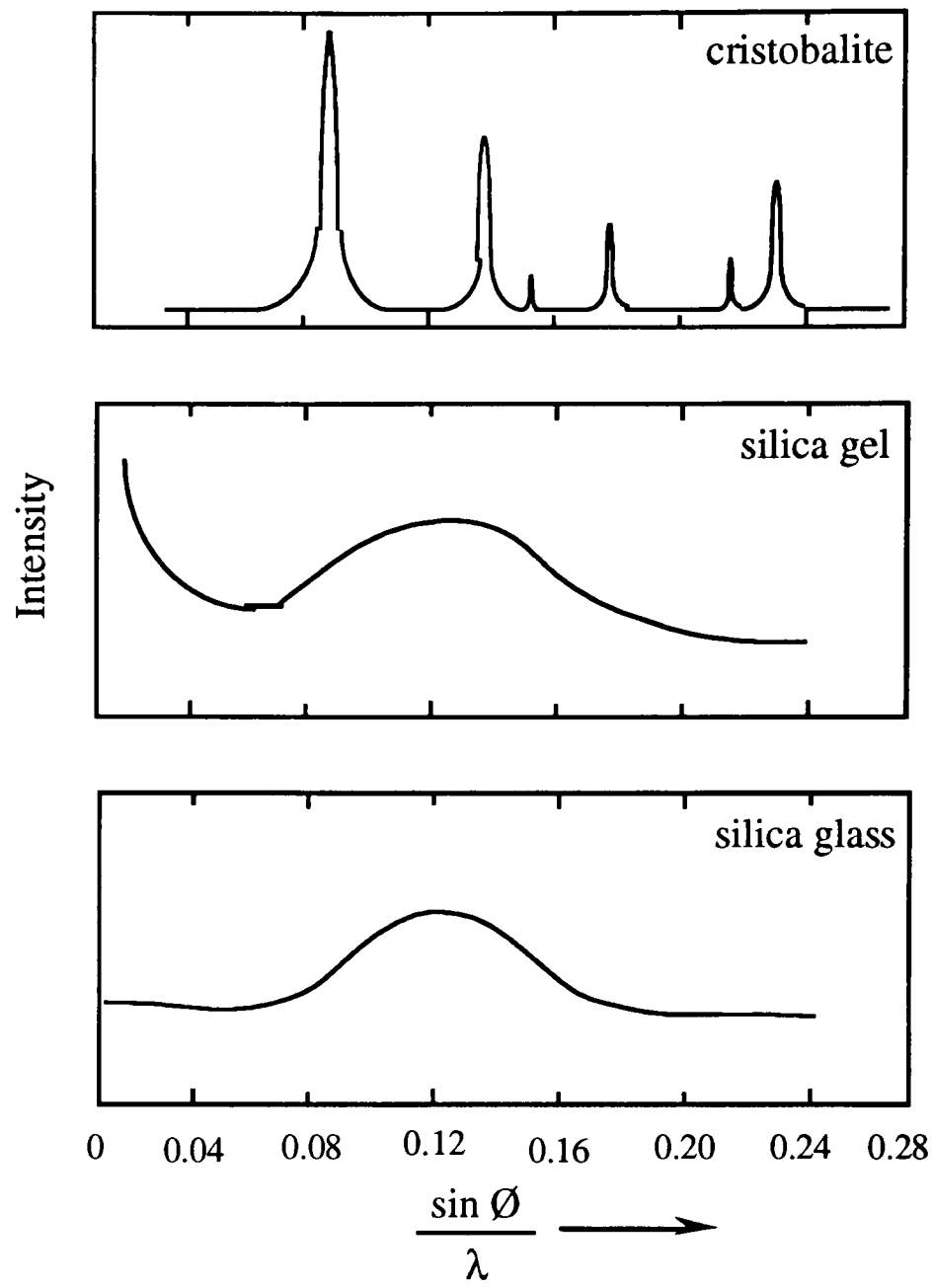


Figure 16: X-ray diffraction patterns of cristobalite, silica gel and vitreous silica[38]

2.4: Colloidal Chemistry

2.4.1: Definition

The word colloid was introduced by Thomas Graham[43] in 1861 and is derived from the Greek word "κωλλα" which means 'glue'. As such, colloid chemistry literally means 'glue chemistry'.The term is defined as the physical chemistry of two phase systems, one of the phases being dispersed to so-called 'colloidal dimensions' within the other phase. The colloidal dimensions lie within arbitrarily chosen limits of between 10 and 10^4 Angstroms (1 to 1000 nm in at least one direction).

It is not necessary for all three dimensions to lie within the colloidal range, since colloidal behaviour can be observed in systems containing fibres in which only two dimensions are below 1μm. The

upper limit depends upon the system, usually being the maximum size of particle which will not settle out of the suspending medium. The dispersed particles may be small solid particles, macromolecules, small droplets of liquids or even small gas bubbles. The continuous phase may be a solid, liquid or a gas. The range of colloidal systems used for practical applications is wide, as is the range of processes which utilise the colloid/surface chemical phenomena to some extent. Examples of processes which rely upon colloid chemistry are[45]:

Adhesion	Chromatography
Ore flotation	Precipitation
Detergency	Road surfacing
Electrophoretic deposition	Emulsion polymerisation
Food processing	Grinding
Heterogeneous catalysts	Ion exchange
Lubrication	Oil-well drilling
Sewage disposal	Soil conditioning
Sugar refining	Water clarification
Water evaporation control	Water repellancy
Wetting	

2.4.2: Classification of Colloidal Systems

Colloidal systems may be grouped into three general classifications:

1. **Colloidal Dispersions** - thermodynamically unstable owing to their high surface free energy and are irreversible systems in the sense that they are not easily reconstituted after phase separation

2. **Macromolecular Colloids** (natural or synthetic) - are thermodynamically stable and reversible in the sense that they are easily reconstituted after separation of solute from solvent

3. **Associated Colloids** (sometimes referred to as colloidal electrolytes) - which are thermodynamically stable

Colloidal Dispersions

The particles in a dispersion are sufficiently large for definite surfaces of separation to exist between the particles and the medium in which they are dispersed. Simple colloidal dispersions are therefore two-phase systems. The constituents are distinguished by the term 'dispersed phase' for the phase forming the particles and 'dispersion medium' for the medium in which the particles are dispersed. Examples of dispersion colloids are shown in Table 5. Sols and emulsions are by far the most important type of colloidal dispersion. The term sol is used to distinguish colloidal suspensions from macroscopic suspensions even though at times the boundary is unclear.

A characteristic feature of dispersions is the large area-to-volume ratio for the particles involved. At the interfaces between the particles and the continuous phase surface properties, such as adsorption and electric double layer effects, are evident and play an important role in determining the physical properties of the system as a whole. It is the material closest to this interface which exerts the greatest influence on the particle-particle and particle-medium interactions.

Dispersion colloids in which the continuous phase is a liquid are often referred to as hydrophobic[46]. The term hydrophobic ('water hating') suggests that the material repels water (or in general the solvent) and suggests that wetting of the particle surface by the solvent does not take place. However, wetting does take place and several monolayers of water are usually absorbed on the surface of the particles. Historically the term is used to distinguish between colloid classifications[46] and usually refers to particles that have been produced by mechanical or chemical action.

Macromolecular Colloids

Macromolecular colloidal systems consist of a dispersion of very large particles within a solvent. The particles are either macromolecules of considerable length which even when coiled up have diameters of well over 1 nm, or aggregates of smaller molecules forming micelles of a size falling within the colloidal range[44]. Macromolecular chemistry covers a wide field which includes the following substances:

Proteins	Cellulose
Gums	Natural rubber
Rayon	Sodium carboxymethyl cellulose
Vulcanised rubber	Polyethylene
Teflon	Polystyrene
Perspex	Terylene
Nylon	Jellies
Glue	

High polymers contain giant molecules which are built up from a large number of similar (but not necessarily identical) units linked by primary valence bonds. These long chains are dispersed in a solvent to form a colloidal suspension. The colloidal properties of such solutions are the result of the large size of the dispersed molecules with respect to the size of the molecules in the liquid medium.

Macromolecular colloids are often referred to as 'hydrophilic' or 'water lovers'. This refers to the tendency of the particles to attract water and become highly solvated. In solutions of long thread-like polymer chains cross linking occurs and a three dimensional network is formed. If all of the solvent becomes mechanically trapped and immobilised within this network, the system as a whole takes on a solid appearance and is called a gel.

CLASS	EXAMPLES	DISPERSE PHASE	DISPERSION MEDIUM
Liquid aerosol or aerosol of liquid particles[a]	Fog, mist, tobacco smoke, 'aerosol sprays'	Liquid	Gas
Solid aerosol or aerosol of solid particles[a]	Industrial smokes	Solid	Gas
Emulsions	Milk, butter, mayonnaise, asphalt, pharmecutical creams	Liquid	Liquid
Sols or colloidal suspensions	Inorganic colloids (gold, silver, iodide, sulphur, metallic hydroxides etc), paints[b]	Solid	Liquid
Paste (when conc.)	Clay slurries, toothpaste, muds, polymer lattices	Solid	Liquid
Solid suspension or dispersion	Opal, pearl, stained glass, pigmented plastics	Solid	Solid
Foam[c]	Froths, foams	Gas	Liquid
Solid foam	Meerschaum, expanded plastics	Gas	Solid
Xerogels[d]	Microporous oxides, 'silica gel', porous glass, microporous carbons, zeolites	-	-

Table 5: Examples of dispersion colloids[44]

[a] preferred nomenclature

[b] many modern paints are more complex

[c] in a foam it is usually the thickness of the film of dispersion medium which is of colloidal dimensions

[d] In some cases both phases are continuous

Association Colloids

The formation of colloidal dispersions by growth from the molecular state is often controlled by a nucleation step. However, with association colloids nucleation is absent and growth of the particles is spontaneous. The structures formed are limited by geometric and energy factors and have sizes often towards the lower end of the colloid range. Examples of association colloids are soap solutions, detergent solutions and dye solutions, all of which consist of a suspension of micelles in a solvent medium. The term micelle is used to describe the small aggregates formed from molecules of soap or surface active ingredients. Miscelles appear only beyond a certain minimum concentration known as the critical micellization concentration.

Surface active substances consist of molecules containing two parts; one which is highly soluble in the dispersion medium (hydrophilic) and and the other which is insoluble (hydrophobic). The molecules come together to form a structure which will minimise contact between the hydrophobic part of the molecule and yet retain maximum contact between the hydrophilic part and the solvent. One such structure is the spherical miscell (Figure 17), which satisfies the geometric constraints imposed by the individual molecules. There are many other types of miscelle such as disc-like, cylindrical, lamellar and spherical vesicles[44].

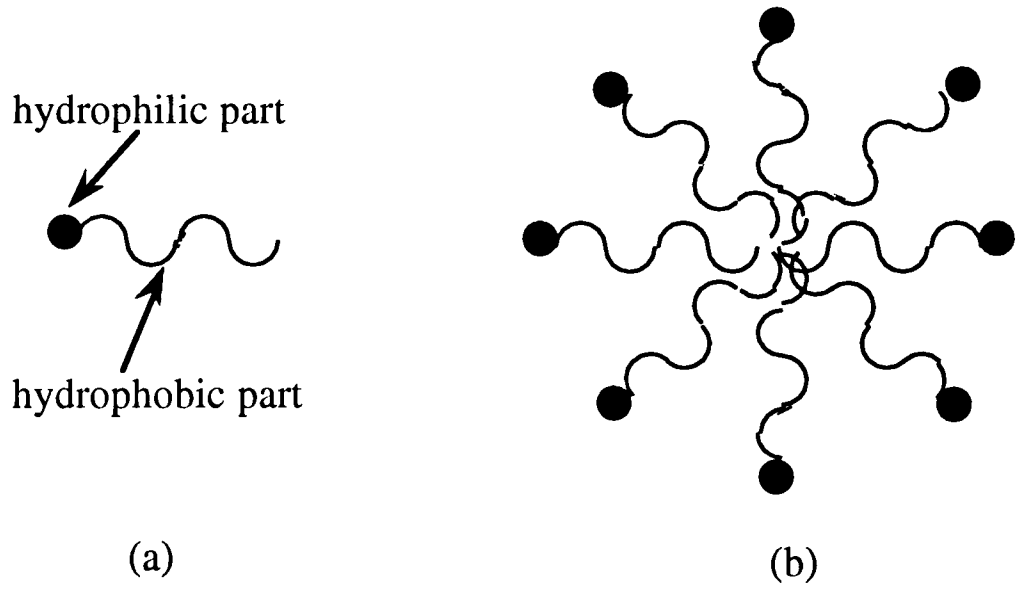


Figure 17: The formation of a spherical miscelle
(a) constituent molecule
(b) miscelle

2.4.3: Colloid Stability

The stability of a colloidal system is the ability of the particles to remain in suspension without flocculating or coagulating. The particles remain dispersed within the solvent because of two basic physical principles; interparticle repulsion and electrostatic forces. When the correct balance is reached the particles remain suspended in the liquid until an outside influence alters the individual forces and sedimentation occurs.

Interparticle Forces

The existence of attractive forces between non-polar molecules was first investigated by van der Waals in 1873 but their origin was not understood until 1930 when London showed how they could be calculated using quantum mechanical theories[44]. According to theoretical calculations, attractive forces between the particles increase as they approach one another (Figure 18).

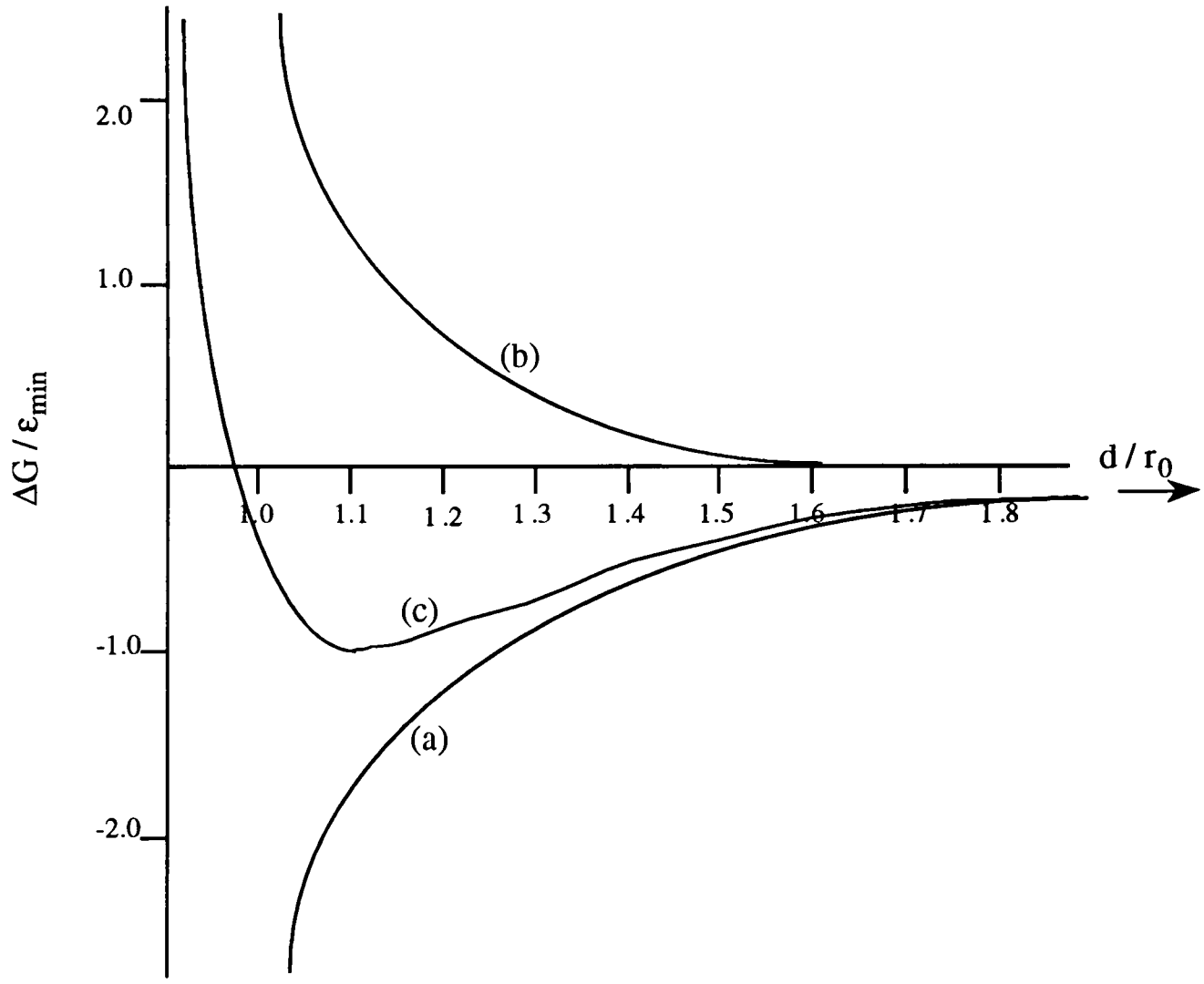


Figure 18: Potential energy of interaction, ΔG(d), between two molecules a distance d apart[44]
(a) van der Waals attraction
(b) Born repulsion
(c) resultant intermolecular potential

The attractive force increases and the free energy becomes increasingly negative as the atoms approach one another. However, at close distances the electron clouds begin to interact. If the electrons are in non-bonding orbitals a repulsive force is set up. The free energy increases to infinity as the electron clouds interpenetrate. This repulsive force is known as the Born repulsion. The actual potential energy is a combination of this attraction and repulsion and is at a minimum when the particles are at a specific distance from each other. Since any system is stable at the point of lowest energy, the colloid particles will settle at this distance from each other in a stable energy configuration.

Electrostatic Forces - The Electrical Double Layer

Most particles in colloid dispersions carry an electric charge. Surfaces become electrically charged by a variety of mechanisms such as ionisation of surface groups, differential solution of ions from the surface of a sparingly soluble crystal, isomorphous substitution or specific ion adsorption. As such, an ionic atmosphere is developed around a charged colloid particle. This atmosphere is called the electrical double layer[44]. This concept was introduced by Helmholtz, who envisaged an arrangement of charges in two parallel planes as shown in Figure 19. The charge on the particle is distributed over its surface and is just balanced by the total charge in the double layer in which there is an excess of oppositely charged ions (counter-ions). The electrical potential in the solution then falls off exponentially with distance from the surface (Figure 20).

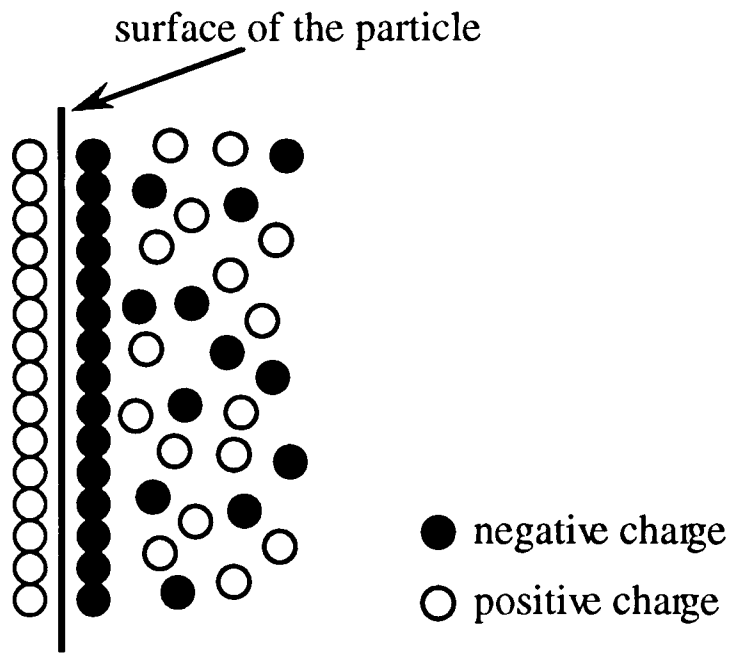


Figure 19: The electrical double layer according to the Helmholtz model[44]

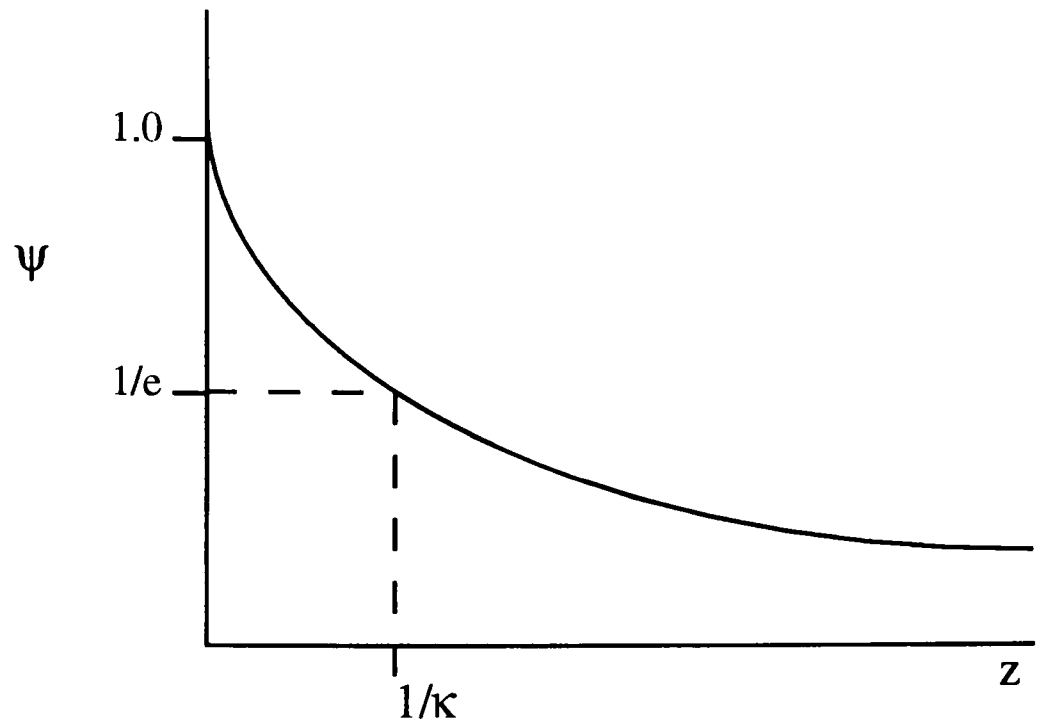


Figure 20: Variation of electrical potential with distance from the surface[44]
1/κ is called the thickness of the double layer

When two similarly charged colloid particles approach one another there will be interaction of the electrical double layers. This results in electrical repulsion between the particles and they will come to rest at the distance where this repulsion is lowest. As such the colloids are held in suspension.

2.5: Colloidal Silica Sols

2.5.1: Definition[47]

The term 'colloid chemistry' is defined as the physical chemistry of two phase systems, one of the phases being dispersed to so-called 'colloidal dimensions' within the other phase. Colloidal silica or a silica sol, may be therefore defined as 'a dispersion of silica in a liquid medium, in which the particle size of the silica is within the colloidal range'.

2.5.2: History

The precursors of colloidal silica sols were solutions of polysilic acids prepared by acidifying sodium silicate solutions or by hydrolysing silicon esters at ordinary temperatures. The first pure silica sols were prepared by Thomas Graham in 1861[48], by dialysis of a neutralised solution of sodium silicate. Various other 'sols' were subsequently produced by methods such as the removal of sodium

from sodium silicate by electrodialysis[49], the liquefaction of gelatinous silica with an alkali[48] and the electrolysis of sodium silicate[50]. Unfortunately, no distinction was made between polysilic acids of low molecular weight and discrete particles of colloidal amorphous silica, and many of these early 'sols' consisted of highly hydrated three-dimensional polysilic acid molecules.

The status of colloidal silica up to 1930 was reviewed by Treadwell and Wieland[51]. Only rarely could a silica sol containing more than 10% silica (by weight) be obtained; such sols were so unstable that they gelled at the slightest disturbance. It was because of the small particle size (< 2-3 nm) that stable concentrated sols could not be obtained.

Colloidal silica did not find wide commercial use until stable concentrated sols, that did not gel or settle out for several years, became available in the 1940's[52]. Control of particle size, pH and the elimination of impurities were the important variables which were brought under control. In 1941, Bird[53] patented a process for removing the alkali from a dilute solution of sodium silicate to produce a stable sol with particle size 5-10 nm in diameter, containing 15-20% silica (by weight). However, it was the process developed by Bechtold and Snyder in 1951[54] that first provided stable concentrated colloidal silica sols of any desired particle size from 10 to 130nm in diameter.

Further refinements by Alexander[55,56] led to the production of stable silica sols with particles only 8nm in diameter, and yet containing more than 30% silica (by weight). Alexander demonstrated that, in order to produce a stable concentrated sol, it was necessary to remove the soluble salts from the dilute sols being produced at the time. By employing a method involving the precipitation of the sol particles by coagulation with polyvalent metal ions, he washed and repeptized the particles to produce stable sols with more than 30% silica (by weight). The same method was also used to control the particle size, degree of aggregation, purity and the optimum concentration of stabilising alkali.

Thus, methods were developed for making discrete silica particles covering the whole range of colloidal sizes and stabilising these as concentrated commercial sols. New types of commercial silica sols have rapidly become available, while others have become obsolete, due to constantly changing developments and demands. Almost all commercial sols contain silica particles 5-50nm in diameter in concentrations of 10-50% by weight. Most are stabilised by an alkali; either sodium hydroxide or ammonia, with a pH between 8 and 10. Some sols are stabilised at low pH by replacing the water with a polar organic solvent or by using alumina particles absorbed on the surface of the silica particles (this gives the particles a positive charge which lowers the free energy of the surface interface and prevents coalescence of the particles)[52]. All commercial sols consist of discrete particles without any appreciable degree of aggregation.

2.5.3: Methods of Preparation

Many processes have been proposed, and are used, for the production of colloidal silica sols. In order to produce sols that are stable at a reasonably high concentration, the particles have to be grown to a certain size under alkaline conditions where they are negatively charged and do not flocculate or gel. The following passage is a summary of the basic methods employed to produce silica sols.

1. Neutralising soluble silicates with acids - a dilute solution of sodium silicate is partly neutralised and silicic acid is deposited on the resulting silica nuclei to form the sol[57,56].

2. Electrodialysis - sodium silicate is passed over a Pb anode (in sulphuric acid) and a steel cathode (in sodium hydroxide) to deposit silica onto a solution of silica nuclei prepared by method 1[58].

3. Ion Exchange - silica sols are made by passing hot dilute sodium silicate solution through an ion exchange resin to produce an acidic sol which is then grown by passing the sol nuclei through a weakly alkaline aqueous medium containing sodium silicate. Liberated silica is deposited on the sol particles, thus increasing their size[59].

4. Peptising Gels - a silica gel is formed under alkaline conditions by incomplete neutralisation of sodium silicate. The gel is then washed and heated in water at elevated temperature and pressure to liquefy the silica and produce a sol[60].

5. Hydrolysis of Silicon Compounds - very uniform spherical silica particles of almost any desired size up to 1 micron are made by hydrolysing a lower alkyl silicate in an alcohol medium containing suitable amounts of water and ammonia[61]. Sodium silicate can be hydrolysed if sufficiently diluted and treated in an autoclave[62].

6. Dissolution of Elemental Silicon - pulverised silicon metal is treated with hydrofluoric acid to remove the oxide film and reacted with water in an alkaline medium (particularly ammonia), to form colloidal silica which is stabilised by the alkali[63,64].

7. Dispersion of Pyrogenic Silica - silicon tetrachloride is burnt with natural gas to form hydrogen chloride and silicon dioxide vapour. In the presence of this reducing agent, silicon monoxide (SiO) is formed which condenses in an extremely divided powder form. This powder is then dispersed in a liquid medium to form a sol[52].

2.5.4: The Uses of Colloidal Silica

Colloidal silica found no consistent uses until concentrated, standardised, stable sols became commercially available. Since that time, colloidal silica has been used for a wide variety of purposes and many new applications are being found. Some of the more important uses are summarised below:

1. Making silica gels, whose surface area, pore size and mechanical strength are determined by the particle size of the precursor colloidal silica, for use as catalyst bases and absorbents[65].

2. Stiffening and binding fibrous[66] and granular[67] materials by incorporating the sol and drying the materials to a rigid gel structure, for example, precision casting moulds[68], moulded refractory products[69] and high temperature insulating materials[70].

3. Increasing the coefficient of friction of surfaces ('invisible sand'), for example, railway tracks[71], waxed floors[72] and textile fibres[73].

4. Polishing agent for silicon wafers, metals and ceramics[74].

5. Adsorbed coatings on surfaces; optical effects[75].

6. Photography; component in multilayer film systems[76].

7. Refractory glasses made with small amounts of alkali - the 'sol-gel' process[77].

2.5.5: The Gellation Behaviour of Silica Sols

The gellation of a silica sol is the formation of a coherent, rigid, three dimensional network of continuous particles of colloidal silica[52]. The initial step in gel formation is the adhesion of closely packed silica particles of low surface charge, with the formation of siloxane bonds which hold the particles irreversibly together. In water based sols, all the particles are sufficiently negatively charged to prevent the particles from colliding and so keep the sol stable[18]. However, if the negative charge is reduced, for example by decreasing the pH, adding an electrolyte or concentrating the silica by evaporation of the water (Figure 21), the silica particles will come into contact and polymerise. A summary of the bond formation between the silica particles is shown in Figure 22.

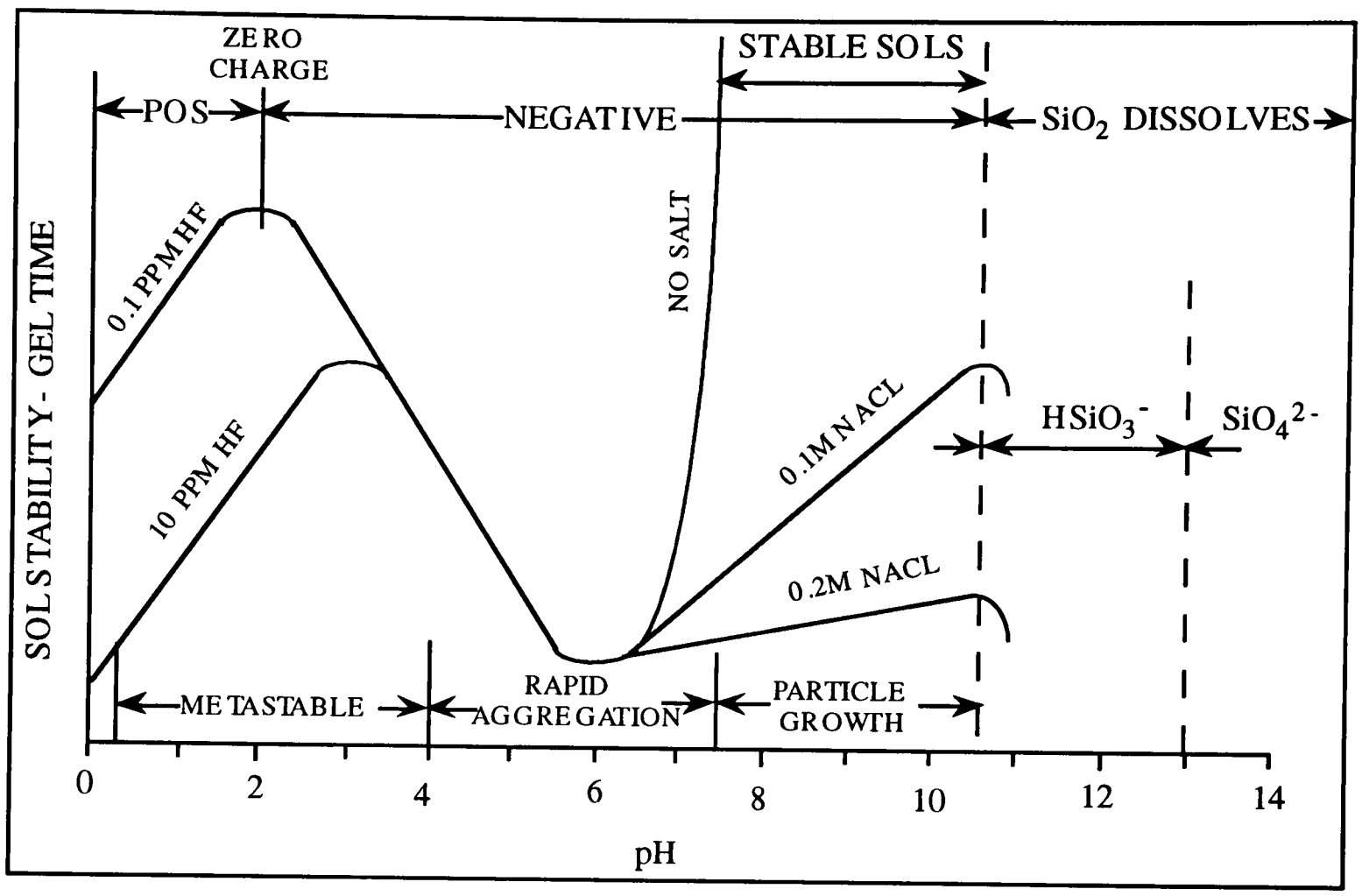


Figure 21: Effects of pH in the colloidal silica-water system[38]

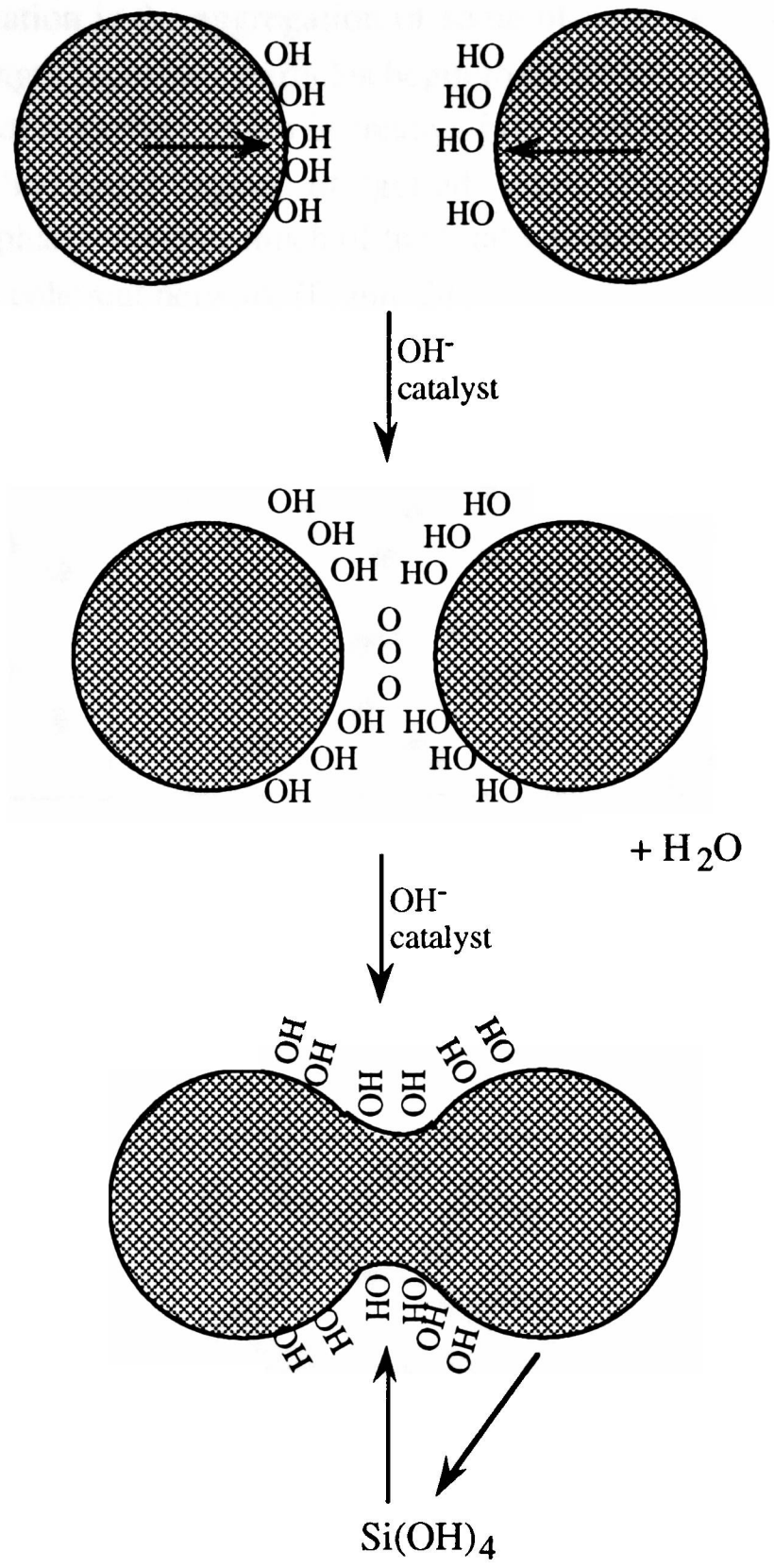


Figure 22: Bond formation between silica particles[38]

With little or no charge repulsion, collision results in formation of interparticle siloxane bonds, catalyzed by base ions. Once bonded, the particles grow together.

The next step in gel formation is the aggregation of some of these polymerised particles into short chains[52]. As the chain length increases, particles begin to be added to both the sides and the ends of the chains. Thus a region of branched chains is created. Free particles within this region are added to the network, forming a 'microgel region' of 'gelled' silica (Figure 23). Each microgel region increases in size until gel phase occupies much of the total volume. At this point the gel regions grow together into a continuous coherent network (Figure 24).

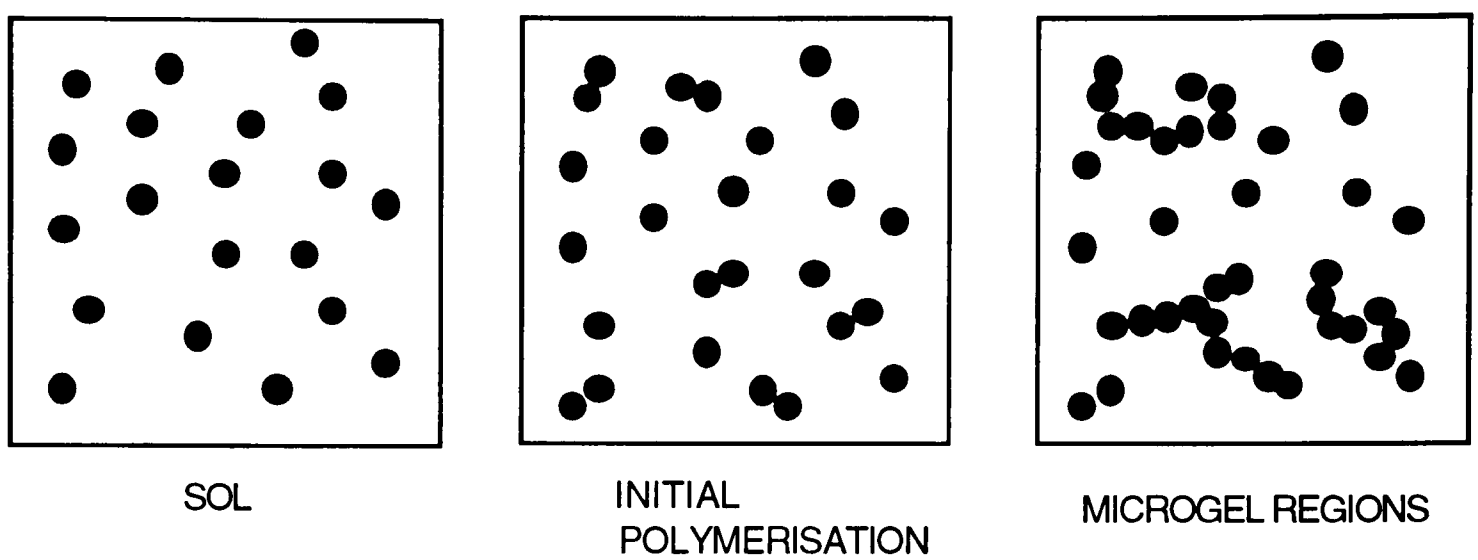


Figure 23: Two dimensional representation of microgel formation.

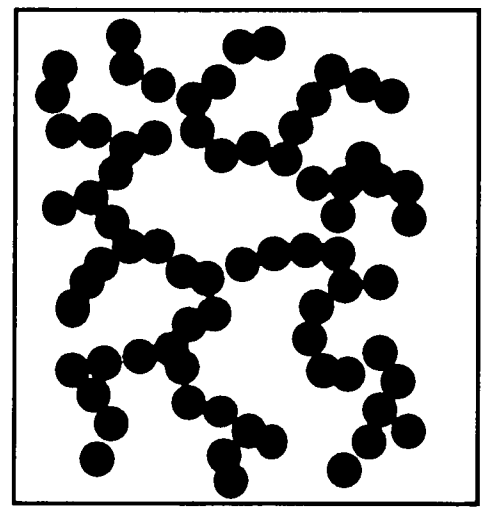


Figure 24: Two dimensional representation of the final gel structure.

The gel network has now been formed but the structure is still quite flexible. The particle-particle bonds are strengthened by partial coalescence in the crevices at the points of contact (Figure 22). The silica particles then grow together because the solubility of silica in these regions is less than that of the silica over the surface of the particle[52]. The resulting fibrillar gel structure is shown in Figure 25.

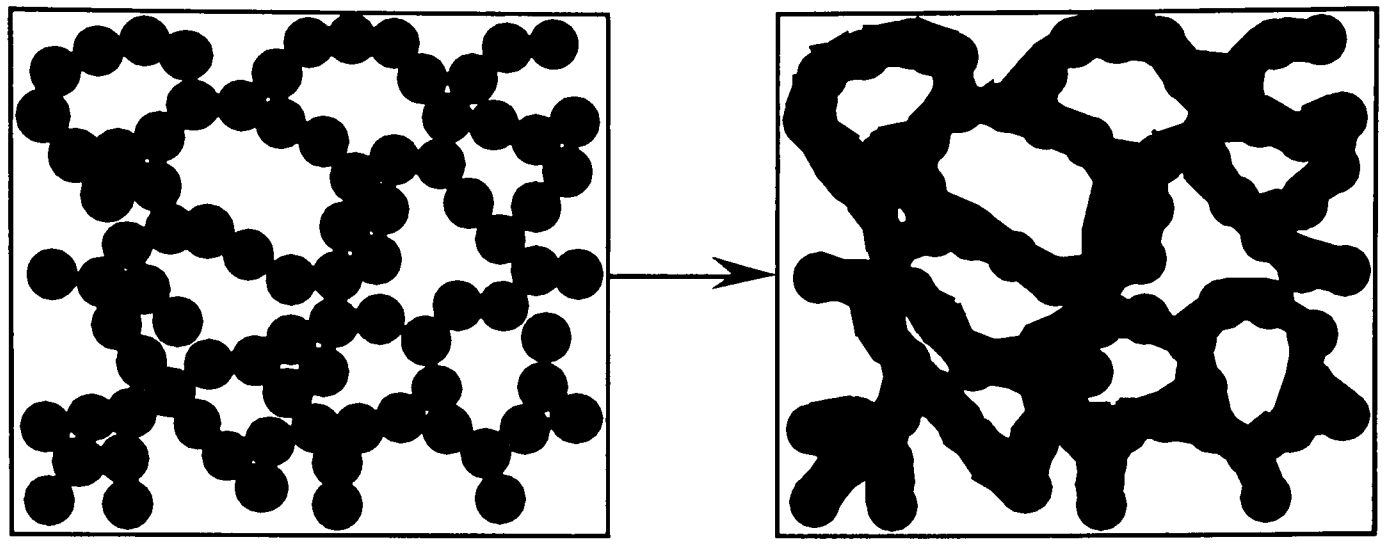


Figure 25: Two dimensional representation of a dilute gel converted to 'fibrils' by silica rearrangement.

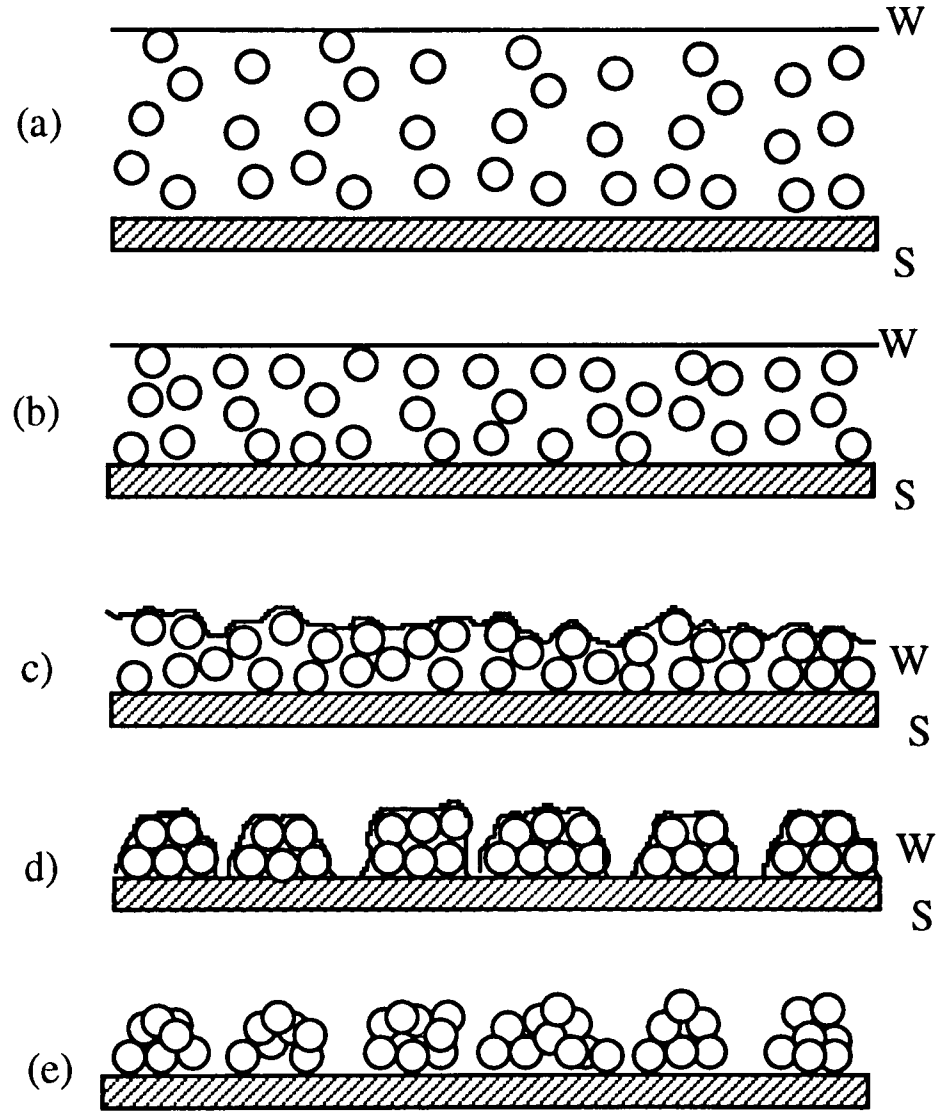


Figure 26: Evaporating a film of silica sol to gel and drying: schematic cross-section[52] (a) sol (b) concentrated sol-beginning of aggregation (c) gel compressed by surface tension (d) fracturing of gel by shrinkage (e) dried loose gel fragments
W=water surface S=solid substrate

As further water is removed from the gel network, three-dimensional shrinkage occurs. This is due to a compressive surface force being developed by the water remaining in the capillaries of the gel which induces stresses within the network that can produce fractures. A gel produced from a sol of uniform particle size has an open network structure containing large pores which act as capillaries (Figure 26). This gel is more likely to fracture than one made from a sol containing a mixture of large and small particles (Figure 27), which contains fewer capillaries.

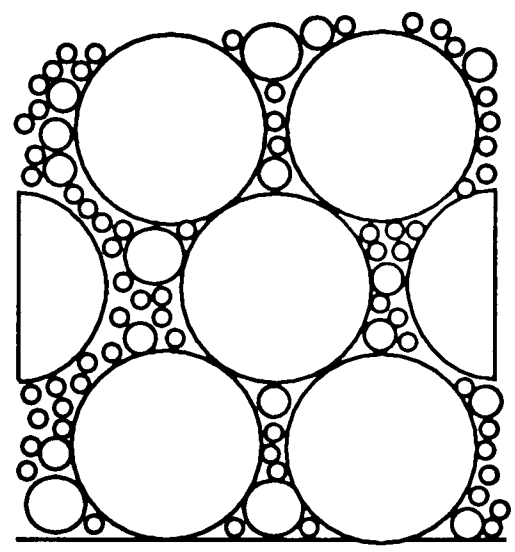


Figure 27: Strong, dense gel is formed from a mixture of large and small particles

2.5.6: Sintering of Silica Gels in Air

Sintering is the removal of pores from a silica gel by the application of heat. The first stage, up to 300°C, mainly involves loss of water from the pores and is referred to as 'activation', since afterwards the gel has a higher adsorption capacity. From 300-600°C, more water is lost by dehydration of surface silanol groups but there is little, if any, change in the surface area or pore structure[52]. Stronger bonds do, however, develop at the contacts between the particles as there is an increase in the coalescence factor.

Sintering of the gel begins at 600-700°C[47]. A study conducted by W.O. Milligan[78], into the effects of elevated temperatures upon the structure of a silica gel, showed that samples heated for two hours at temperatures between 200 and 1000°C showed no evidence of crystallinity. Slight sintering occurs at 650°C, while a more rapid loss of surface area occurs at higher temperatures. At still higher temperatures, the specific surface area decreases, the gel shrinks, and the pore volume decreases but the size of the remaining pores usually remains the same. In similar studies[79], silica gel heated from 100 to 1000°C showed no change in pore diameter, although the surface area had decreased and the density increased.

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It appears that pores of all sizes are destroyed in the same manner as the silica is converted from the porous to the non-porous state, without the size of the remaining pores undergoing any change. One explanation for this phenomenon is that there could be localised impurities such as sodium ions around some pores which promote sintering enabling these particular pores to disappear leaving others of the same size unchanged. However, this now appears unlikely since a study carried out on ion-free silica exhibited the same behaviour[80].

The rate of heating and the range of particle sizes within the gel also affect the sintering behaviour. If a sample of silica gel is suddenly heated to a high temperature, the evolved water has a marked catalytic effect and the rate of sintering is increased. If heating is gradual and more water is allowed to escape before the sintering onset temperature is reached, then sintering and loss of surface area is less marked[52]. When all the particles in a gel are of very uniform size and are packed in a uniform manner, most of the pores will be evenly sized and the point at which they all disappear from the structure will be within a small temperature range[52].When the particles are a mixture of sizes, the range of pore sizes will also be wide and pores will disappear over a much wider range of temperatures. At temperatures above 1000°C devitrification may begin by nucleation of crystals of cristobalite. If the gel is very pure[80] devitrification does not occur even after 5 hours at 1400°C. There are interatomic bonding changes within the silica itself even at moderate temperatures although the gel remains X-ray amorphous. It has been shown by infrared absorption that there are small organised domains with structures resembling either quartz, tridymite, or cristobalite[81].

When comparing a silica gel prepared from a sol base with a gel prepared from ethyl silicate[82] it appears that sol based gels crystallise at lower temperatures than ethyl silicate based gels. DTA (see Section 3.3) shows no crystallisation up to 1300°C for an ethyl silicate gel but the crystallisation of a sol gel can be clearly observed[83]. This has been attributed to the small amount of Na_2O used to stabilise the sols, initiating crystallisation at lower temperatures.

2.5.7: The Effect of Impurities

2.5.7.1: Transformations of Silica Minerals

When silica is heated, the tetrahedral units of silica $(SiO_4)^{4-}$ appear to dissociate and be capable of migration. On cooling, they reform around other ions or groups in such a manner as to form the most stable configuration[38]. When quartz is heated, it is converted slowly into tridymite or cristobalite but the addition of other cations can accelerate this conversion. Some cations promote the formation of cristobalite, others tridymite, whilst some (principally Al^{3+} and Ti^{4+}) do not assist the conversion of quartz; indeed alumina retards it. The catalysing effects of various cations are summarised in Table 6.

Table 6: The effect of various cations in catalysing silica

Cation	Ionic radius / Å	z/a^2	Effect
K^+	1.33	0.13	T
Na^+	0.95	0.18	T
Li^+	0.60	0.25	C
Ba^{2+}	1.35	0.25	C
Ca^{2+}	0.99	0.35	C
Fe^{2+}	0.76	0.43	C
Mg^{2+}	0.65	0.47	C
Be^{2+}	0.31	0.68	Q
Al^{3+}	0.50	0.83	Q
Ti^{4+}	0.68	0.92	Q

T=tridymite forming catalyst

C=cristobalite forming catalyst

Q=quartz forming catalyst

z=charge on the cation

r_c=radius of the cation

r_a=radius of the anion

$a=r_c+r_a$

z/a^2=field strength

When such cations are present, the dissociated silica tetrahedra nucleate around them. The different effects of various cations depend upon the sphere of influence, which is best represented by the field strength (z/a^2), which is the charge per unit surface area of a sphere equivalent in size to the sum of radius of cation and anion (Table 6)[84]. Small field strengths will give rise to open silica configurations around the cation due to the charge being smaller, and the silica form produced will be less dense. Tridymite has the most open lattice of the silica minerals; cristobalite is more dense while quartz is the most dense. Cations with small field strengths (K^+ and Na^+) nucleate tridymite and others with larger field strengths nucleate the formation of cristobalite and quartz; e.g. Ba^{2+} and Al^{3+} promote the formation of cristobalite and quartz respectively.

2.5.7.2: Devitrification of Sol Based Silicates

The densification of amorphous silica above 1000°C is strongly catalysed by traces of impurities, especially alkali metals such as sodium, lithium and potassium. The amount of alkali required to promote crystallisation is very small; T_c (the temperature of crystallisation) decreases markedly for the first 0.05 mol% of alkali and then decreases more slowly for additions up to 0.20 mol%[85].

The nature of the crystalline phase varies according to the impurity cation but it should be noted that the same impurity cations do not have the same effect upon a silica gel as they do upon the silica minerals (see Section 2.5.7.1). When incorporated with a silica gel, sodium and potassium promote the formation of cristobalite (as opposed to promoting the formation of tridymite in a silica mineral); and for higher amounts of alkali, small amounts of tridymite can also be detected[4].Lithium promotes crystallisation to quartz; this is probably due to the small radius of the ions which enables them to enter the quartz lattice.

The rate of conversion of amorphous silica to crystalline silica is strongly influenced by the presence of various materials which may serve as crystal nuclei, and by materials which labilize the Si-O-Si bonds, i.e. make the silica structure much more mobile. For example, a gel containing 2% Al_2O_3, heated to 1160°C, gives a much stronger pattern of cristobalite than silica gel containing no alumina[52]. However, if more alumina is present the cristobalite pattern becomes weaker. Large amounts of alumina reduce the mobility of the silica structure preventing crystallisation but small amounts act as heterogeneous nuclei to promote the formation of cristobalite.

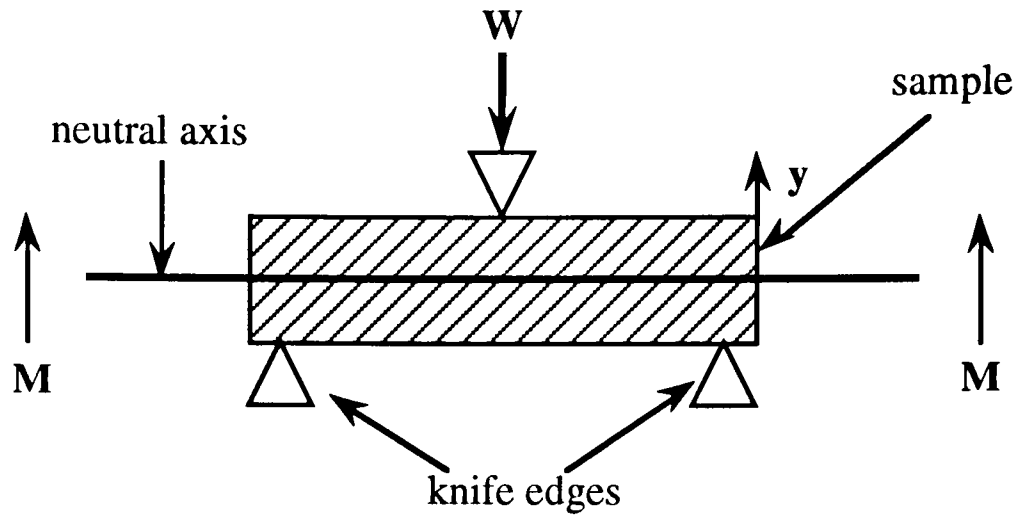
6: Physical Properties

6.1: Three Point Bending

Consider a beam of bisymmetrical cross-section held on supports at the ends and loaded by a constant force (Figure 28). The deformation produces a couple in the plane of symmetry which is called the bending moment (Figure 29). The maximum bending moment (M) is calculated using Equation 6[86] and occurs at x = L/2 i.e. the centre of a symmetrical beam:

$$M = -L\left(F + \frac{wL}{2}\right) / 4$$ **Equation 6**

M = bending moment
L = length of the beam
F = force
w = weight of the beam



y = distance from the neutral axis in the direction of the force

W = load

M = bending moment

σ = stress

neutral axis = plane at 90° to the force at which point nett $\sigma = 0$

Figure 28: Three point bending of a beam.

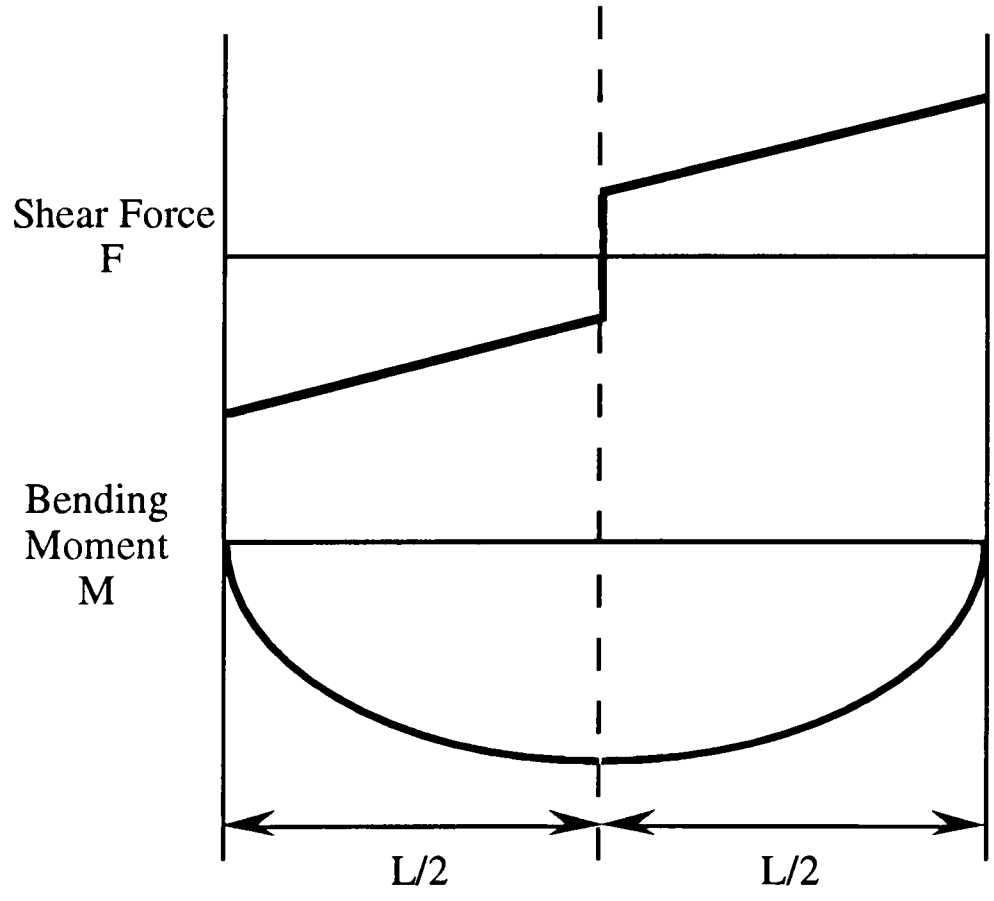


Figure 29: Distribution of shear force and bending moment in the loaded beam of Figure 28[86].

The bending moment in this case is negative and tends to stretch the lower part of the beam and compress the upper. If we assume pure bending with plane sections remaining plane during deformation, then the stress distribution in the beam is shown in Figure 30. As can be seen, one half of the section is loaded in tension and the other half in compression. The maximum extensional stress σ occurs in the upper or lower surface depending upon the sign of the bending moment (where y is at a maximum) and is calculated using Equation 7[86]. Note that this calculation applies to a beam with a rectangular cross section.

$$\sigma = \pm \frac{3\,L}{2ba^2}\,(F + wL/2)$$ **Equation 7**

s = maximum extensional stress
b = width of the beam
a = thickness of the beam
L = length of the beam
F = force acting on the beam
w = weight of the beam

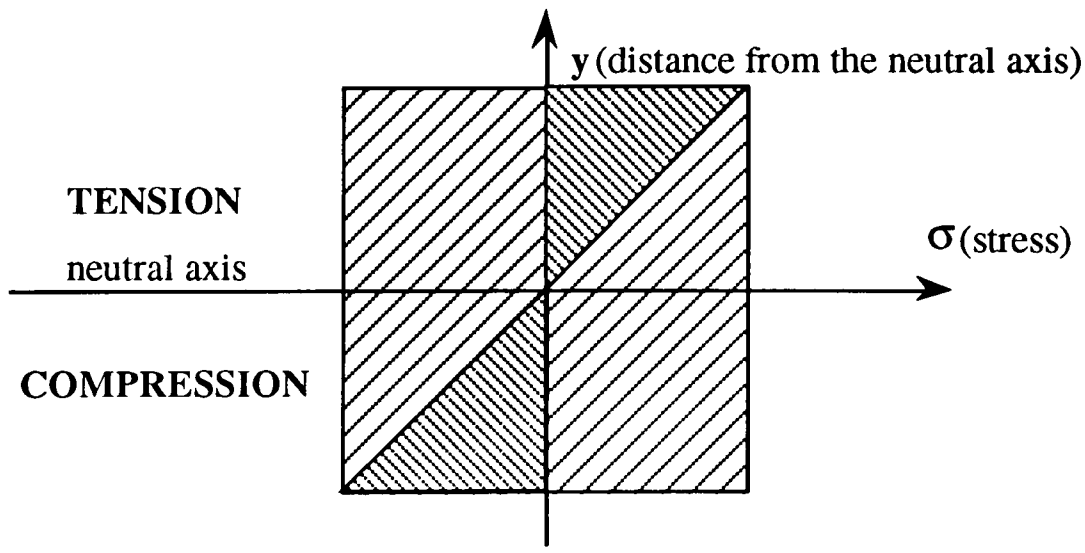


Figure 30: Stress distribution in a cross sectional segment of a rectangular beam during bending.

2.6.2: Creep of Ceramic Materials

Creep is the time-dependent strain that occurs when a material is subjected to a stress for a prolonged period of time[87]. This strain gives rise to slow deformation of solid materials under load. Usually we associate creep with high temperatures, but for large structures with close tolerances even a small nonelastic strain can lead to significant deflection at room temperatures[88].

Ceramics are generally brittle and under tensile stress fracture typically occurs at strains <1%[89]. The fracture strength of a ceramic is dependent upon the temperature and is schematically represented in Figure 31. At low temperatures plastic deformation by slip along certain crystallographic planes is very limited[90] and hence the material acts in an elastic manner up to the stress necessary to cause fracture by propogation of inherent flaws (Region A). Flaws such as pores and surface markings will cause fracture. Slip becomes easier with increasing temperature and the decrease in fracture stress associated with Region B is due to the generation of flaws by plastic deformation. Shear in one grain can nucleate cracks at grain boundaries since the adjacent grain cannot deform to accomodate the strain. To achieve polycrystalline ductility, five independent slip systems must be operating. For most ceramics[91] this only occurs at high temperatures (Region C). Unlike metals, plastic deformation of a ceramic is rarely observed at low temperatures.

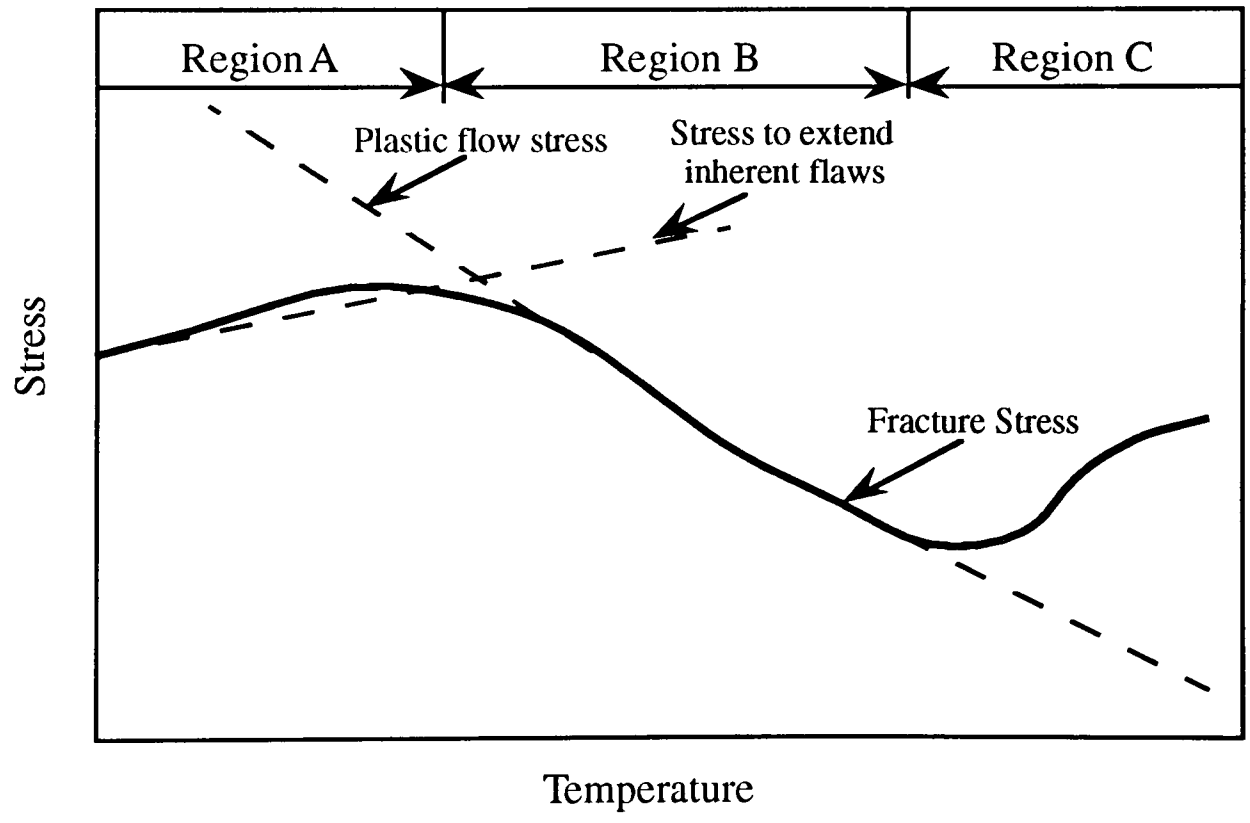


Figure 31: Schematic representation of the fracture strength of ceramics as a function of temperature
Region A: fracture initiates at inherent flaws
Region B: fracture originates at flaws produced by limited plastic deformation
Region C: fracture occurs after considerable plastic deformation[87]

In most applications ceramics are used for their hardness, refractoriness, transparency etc., rather than for their mechanical properties. However, the continual rise in temperatures at which some engineering materials are expected to operate has stimulated interest in the high temperature mechanical properties of ceramics. A number of high melting point ceramics exhibit, at elevated temperatures, better properties than the best superalloys[87]. Thus, some ceramic materials are being considered for use in high performance turbine applications[92]. Similarly, the advanced gas cooled reactor is based upon a uranium oxide/stainless steel fuel pin[93]. Even in traditional ceramic applications such as refractories for furnace linings, creep measurements are being used as an indication of service performance and strength.

Creep of ceramics at temperatures below 0.4 T_m * is rarely encountered and most problems occur at high temperatures where creep can occur at stresses much lower than the fracture stress. Under these conditions the creep strains can be large, the creep rate may vary rapidly with stress and temperature. Deformation can lead to slow crack growth and eventual fracture. It must be noted that the amount of reliable technical information available on the creep of ceramics is very limited, mainly because of the difficulties of testing at elevated temperatures[94].

The creep properties of a ceramic material can be affected by the mode of testing. Relatively few tensile creep studies have been undertaken, due to the low fracture strength in tension and the difficulties of gripping ceramic materials. Consequently, bend or compression tests are usually used, even though the non-uniform stress distribution throughout the specimen with both methods must be taken into account. At low temperatures the tensile strength, modulus of rupture and compression strength of a ceramic material are in the ratio 1 : 2 : 10 [95]. Studies of the creep strength of silicon nitride[94] have demonstrated that the stress required to produce a given creep rate in compression is an order of magnitude greater than that needed in tension. Only with materials that are ductile at the creep temperatures is the creep strength equal in tension and compression. Most ceramic materials when placed under a constant load will experience deflection (Figure 32).

After the initial strain on loading, the normal (transient or primary) stage is found, in which the creep rate decreases continuously with time until a steady-state or secondary stage is reached when the creep rate is essentially constant. Because of the difficulties of obtaining reliable strain readings for ceramic materials, most creep studies have been carried out in the steady-state region. With engineering ceramics transient strains are usually small and at low strain rates a steady-state can be attained immediately after loading. Often the steady-state creep rate is highly reproducible[94] which contrasts with the variability of ceramics when the strength is determined by flaw size distribution[89].

* T_m = melting temperature

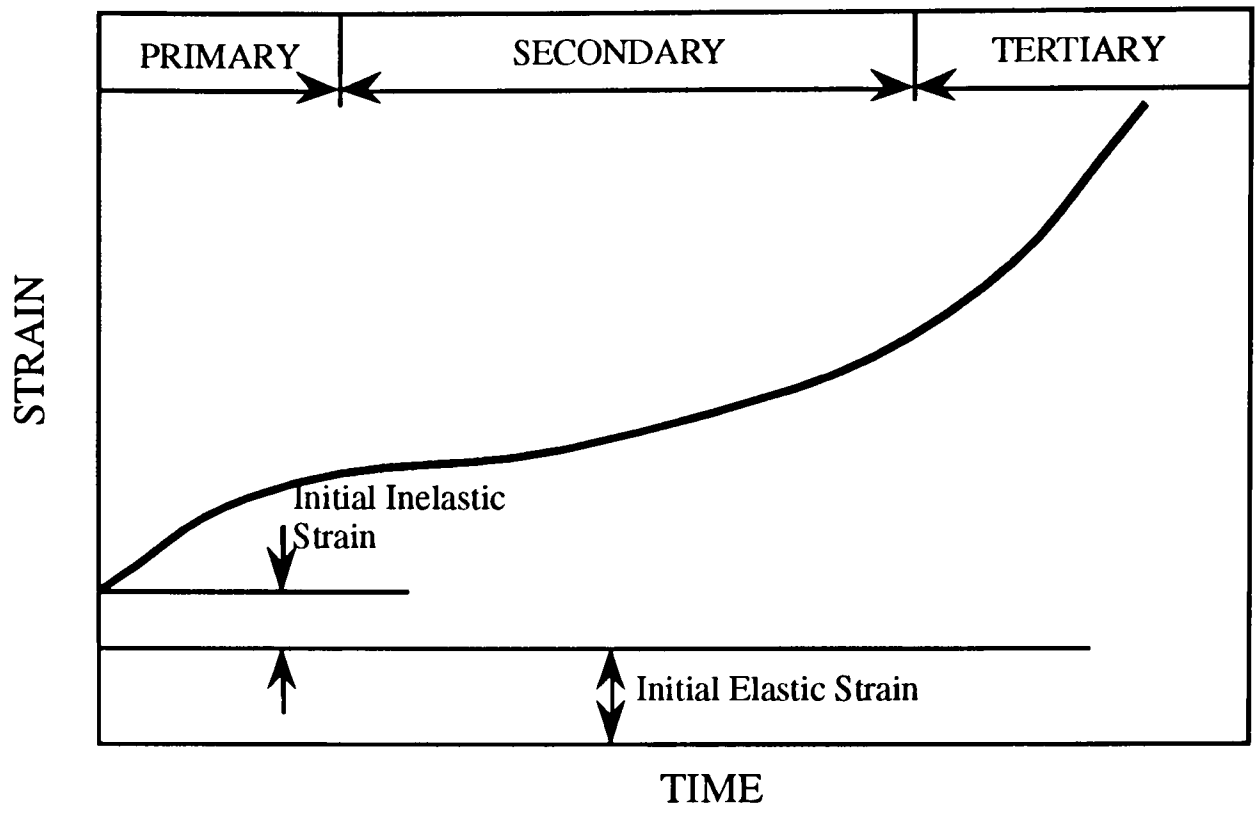


Figure 32: Typical creep curve showing the three stages of creep.

Deflection of the sample during creep is brought about by movement of material within the grain structure. In the primary and secondary stages the creep rate is dependent upon the stress directed diffusion of material from boundaries experiencing normal compressive stress to those under tension. Diffusion occurs through the lattice (Nabarro-Herring creep) and along grain boundaries (Coble creep). The dependence of the creep rate during the steady-state (ε_s) on the applied stress and the temperature during long term tests can be seen in Equation 8. The values of n and Q_c are determined by the type of ceramic and the test conditions.

$$\varepsilon_s = K\,\sigma^n \exp(-Q_c / RT) \qquad \textbf{Equation 8}$$

ε_s = creep rate
K = constant
σ = applied stress
n = constant
Q_c = activation energy for creep
R = Boltzmann's constant
T = temperature

The creep behaviour of a ceramic is influenced by various factors which alter the constants and the activation energy for creep in Equation 8, such as; purity, pore size and distribution, grain size, service environment and temperature.

The steady-state does not continue indefinitely and in most cases the creep rate eventually accelerates in the tertiary stage, leading to fracture. Fracture occurs because of the formation of cavities and cracks at grain boundaries, with the tertiary stage commencing when the cracks have reached a size which affects the creep rate. The cavities and cracks initiate at regions of high stress concentrations such as triple points (where three grains meet) and other irregularities at grain boundaries. In the tertiary stage, material movement occurs by diffusion-controlled generation and movement of dislocations from one crystallographic plane to another.

2.6.3: Refractory Strength Tests

The strength of a material is determined to some extent by its crystalline nature. A homogenous material, as is the case for some metals and single crystals, will rupture by a mechanical tearing apart of the atoms which make up the species. In a composite crystalline material, composed of heterogeneous grains, it is often the grain boundaries which are the source of weakness. Plane contacts permit fracture cracks to initiate and disrupt the atomic order. In a porous material, which is often the case with ceramics and refractories, the various holes and voids are responsible for the initiation of failure. Fracture will invariably follow these defects. so that atomic displacements are not involved. In this case it is the concentration of defects within the structure which determines the ultimate strength of the specimen and not the atomic structure of the base material.

In ceramic materials of a composite nature, fracture rarely occurs across a grain or crystal fragment. More usually the fracture plane follows a complex path, where contact between various mineral phases is at its weakest and particularly where it is possible to link up voids in the structure itself. As such, the strength of the material will be governed by the direction of the applied stress and this must be taken into consideration when measuring this parameter for a ceramic material. A body may break in compression, elongation (tensile stresses), transverse strain, torsion, shear or by impact.

Ceramic and refractory strength tests are therefore designed to measure the properties of the material when fracture occurs in a single mode, with great care taken to eliminate the others during testing. According to the information required, a method exists to determine one or more of the following; tensile strength, compression or crushing strength, transverse strength or modulus of rupture, resistance to impact, torsional strength, modulus of elesticity and hardness or deformability.

1. Tensile Strength

The failure of a body in tension is the least complicated of all the strength tests. A shaped test piece is fitted securely into sample holder of the test machine. Pressure is applied to one face of the test piece to elongate or stretch the sample until fracture occurs. The pressure is applied by a variety of means depending upon the situation. Simple test machines (Figure 33) rely upon a fulcrum method in which the sample is held at one end of a bar and the other end is weighted with a container which is slowly filled with water, sand or mercury. More complex units apply the load by mechanical or hydraulic means. The tensile strength is then simply defined as the pressure applied, per unit cross sectional area, to induce failure. Failure in pure tension involves no applied shear stresses; the sample fractures when the induced strain in the direction of the applied stress becomes too great to be accomodated.

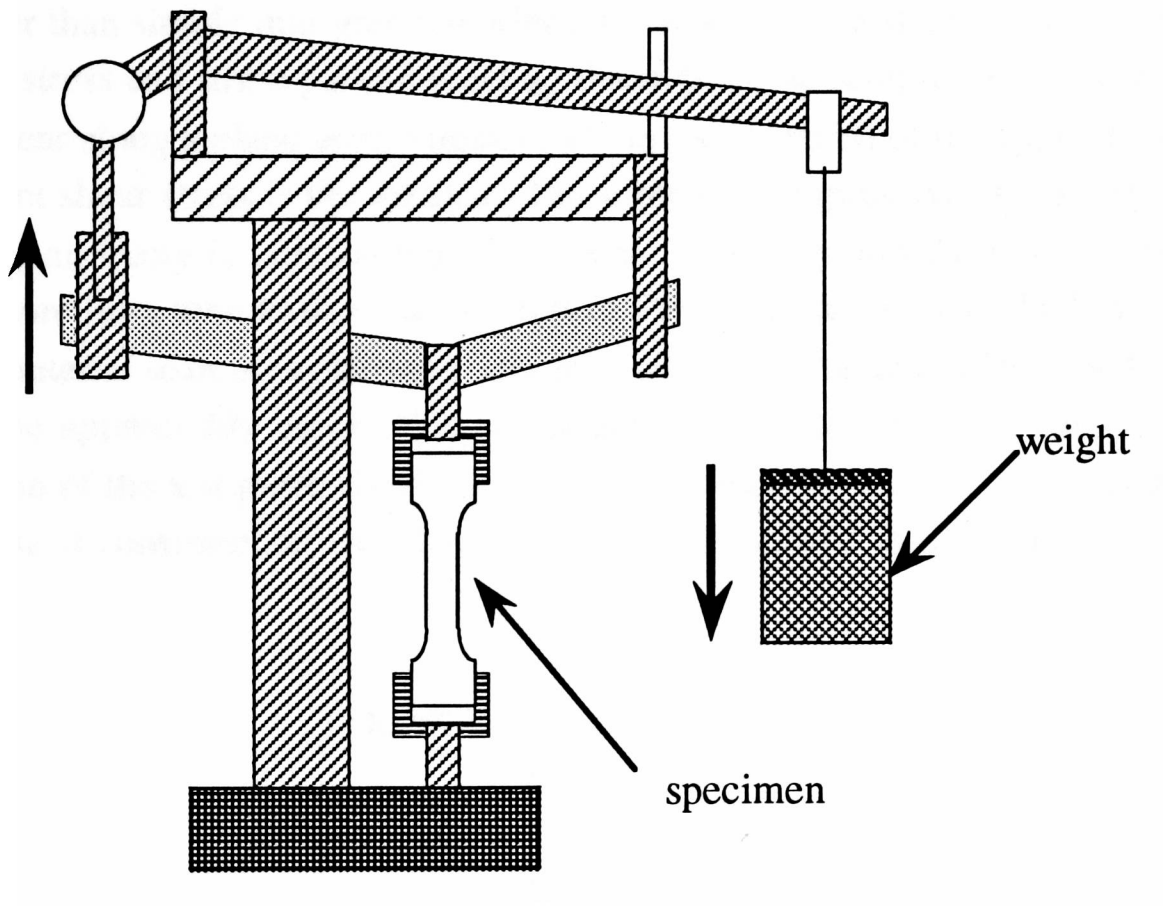


Figure 33: Simple tensile testing machine - showing the sample held in the grips[38]

Sample extension to failure can be measured by placing the two portions of the broken test piece back together and measuring the increase in length. Since this can be difficult with samples which shatter at failure, the same effect is shown by marking two dots, at a known distance apart, onto the sample prior to testing. The distance between these two marks is then remeasured after testing and the difference used to calculate the extensibility.

Simple tensile testing is, however, not an easy procedure. Test pieces of special shape are required so that they can be gripped firmly in place. The test piece must be positioned exactly at right angles to the applied stress or shear and torsional stresses can be induced which will affect the test results. Dried and fired samples need to be prepared and shaped very carefully to ensure that the test conditions are correct. This can sometimes be difficult to achieve with ceramic constituents. It can also be argued that the results are reasonably meaningless since a ceramic component is rarely used in tensile applications. As such, the test tends to be restricted to assessing the green strength of ceramic samples.

2. The Compression Strength Test

Fracture under a compressive stress is complex and the strength determined by this test depends upon many factors other than simple intergranular adhesion. When such a stress is applied to one face of a block, a complex stress and strain pattern is set up throughout the sample. As a result the sample will actually fail by shear along a plane approximately 45° to the direction of the applied stress (Figure 34) where the resultant shear stress is the greatest. The ultimate compressive stress required to produce failure depends upon many factors such as the sample geometry and the rate of application of the stress. Shear fracture lines tend to occur at and follow flaws and cracks, and the large grains found in some refractory material scan act as barriers. Because of this, the sample to be tested must be as large as possible and be appreciably bigger that the largest grains incorporated into the structure. The smallest dimension of the test piece should be at least 10 times bigger than the maximum dimension of the largest grains if consistent and reliable results are to be gained from the test.

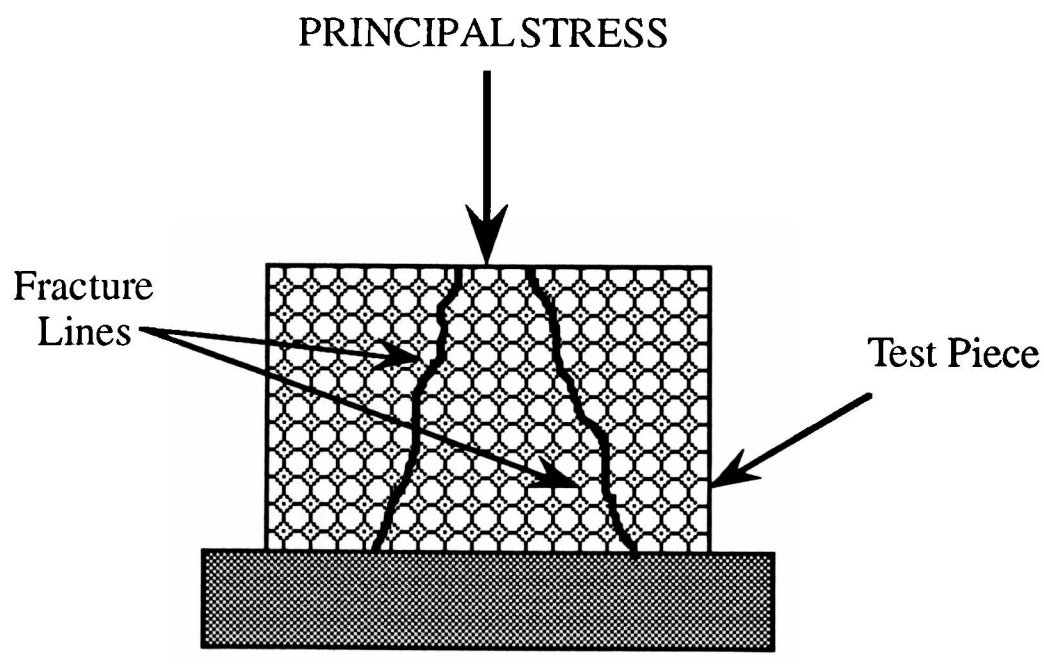


Figure 34: Fracture under an applied compressive stress[39]

Since the measured stress to failure is dependant upon the geometry of the test piece, many equations are required to calculate the compressive strength. Equation 9 is an example of one such calculation, being the empirical relationship used with rectangular samples. The relationship gives fair aggreement for blocks which have an approximately square end section (A). Note that the units of compressive strength are expressed as the pressure applied per unit area of load bearing surface.

$$S_c = S_{co} \left(0.8 + \frac{0.2}{L / \sqrt{A}} \right)$$ **Equation 9**

where S_c = compressive strength
S_{co} = compressive stress for a perfect cube
L = length between the bearer plates
A = area of sample end section

Problems are encountered in compressive testing when the load bearing surfaces are not perfectly flat and rigid. Localised areas of high pressure can be formed on uneven surfaces which can cause premature failure. As such, solid samples are abraded with silicon paper to remove these imperfections before testing.

3. Transverse Tests

Transverse tests are used more frequently than compression or tensile tests, as there is little need for large or expensive apparatus. The test is carried out in the three point bending mode which is less sensitive to either geometry or sample positioning. Often transverse test are referred to as modulus of rupture and procedures are standardised in BS 1902 Part 1A, 1966[38]. A simple apparatus is shown in Figure 35.

In making the test, a test piece is supported upon two 'knife-edges' and pressure is applied by means of a third knife-edge resting on a piece of glass or steel to prevent cutting. The pressure is increased at a pre-arranged rate until the specimen breaks. The load required to fracture the specimen is a measure of the strength of the test piece and is used to calculate the modulus of rupture using Equation 10.

$$T = \frac{3Wl}{2bt^2}$$ **Equation 10**

where T = modulus of rupture
W = breaking load
l = length of the test piece
b = width of the test piece
t = thickness of the test piece

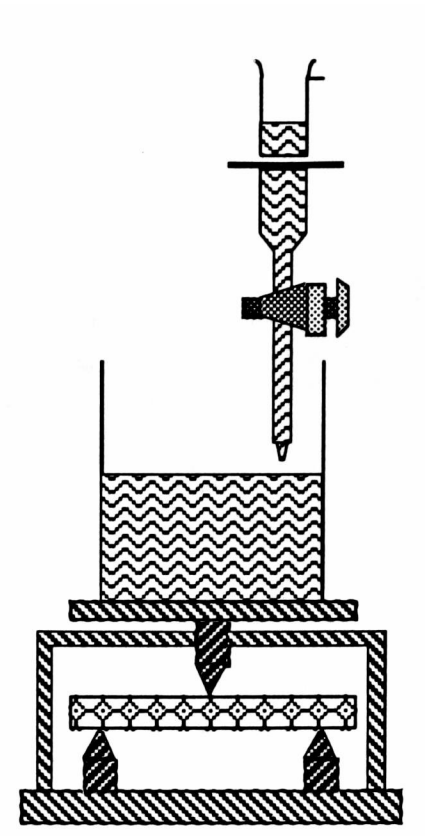


Figure 35: A simple apparatus for measuring the transverse strength of small specimens[38]

This test can be carried out upon both green and fired samples. For specimens of low strength the pressure can be applied by running either water or mercury into a beaker placed on the platform above the third knife edge. Stronger specimens can be fractured by the use of a hydraulic press. It is important, however, that the specimen be straight and free from flaws, otherwise unreliable results can be obtained. This is often difficult to achieve with dried and fired ceramic materials, so at least 10 test pieces must be fractured and compared in order to assess the reliability of the results.

4. Torsion Tests

Torsion testing was developed by Norton[95] in 1948, and has been used successfully for the high temperature testing of refractory materials and as a means to measure the modulus of rigidity. A simple diagram of the apparatus is shown in Figure 36. A specially shaped test-piece, cylindrical in the centre but with square end sections, is clamped at both ends in the torsion head. A torsional load is applied at one end to exert a twisting force on the specimen, which may be surrounded by a furnace if measuring the specimen properties at high temperatures. The load is applied until torsional fracture occurs. Layers of the sample are forced apart but the greatest pressure is on the outside of the test specimen. Tensile stresses develop at an angle to the direction of shear so that failure can often produce a characteristic S-shaped shear fracture line (Figure 37). Torsion tests not only permit the mesurement of the progressive deformation under load, but also the elasticity of the specimen at any desired temperature.

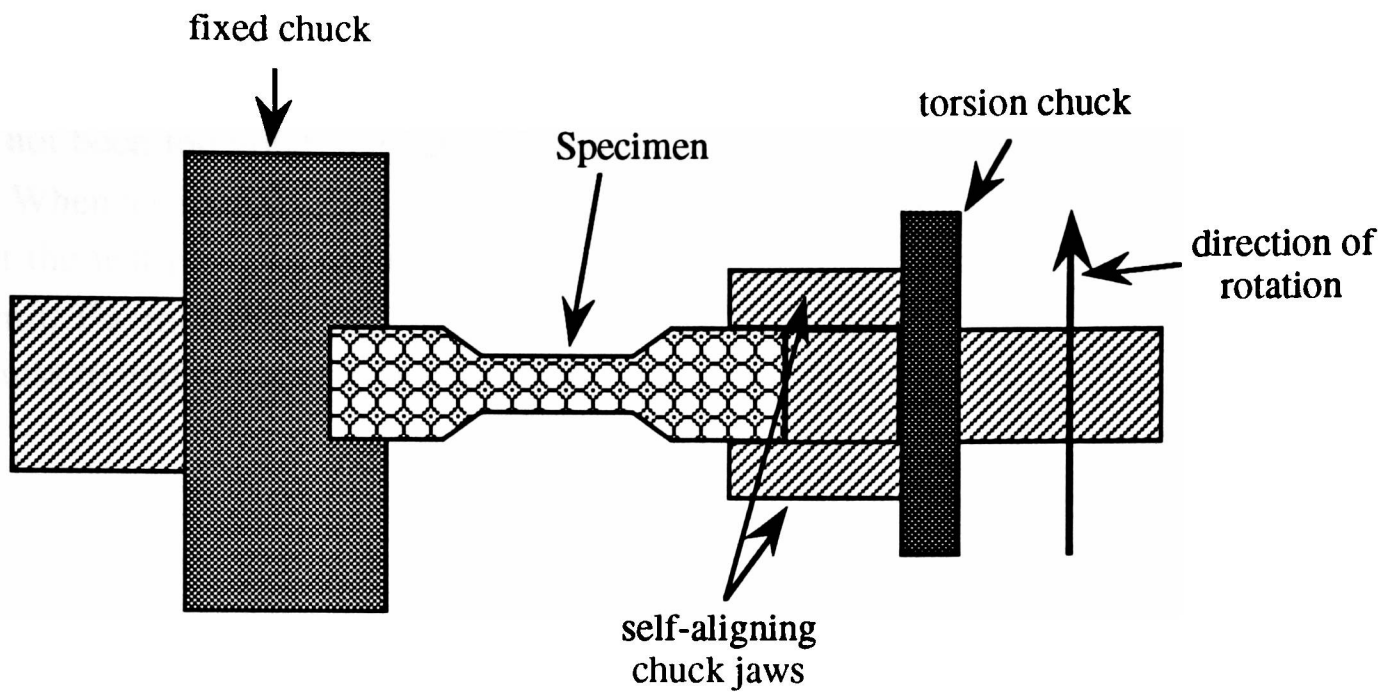


Figure 36: Simple schematic of apparatus for measuring the torsional properties of ceramic materials[38]

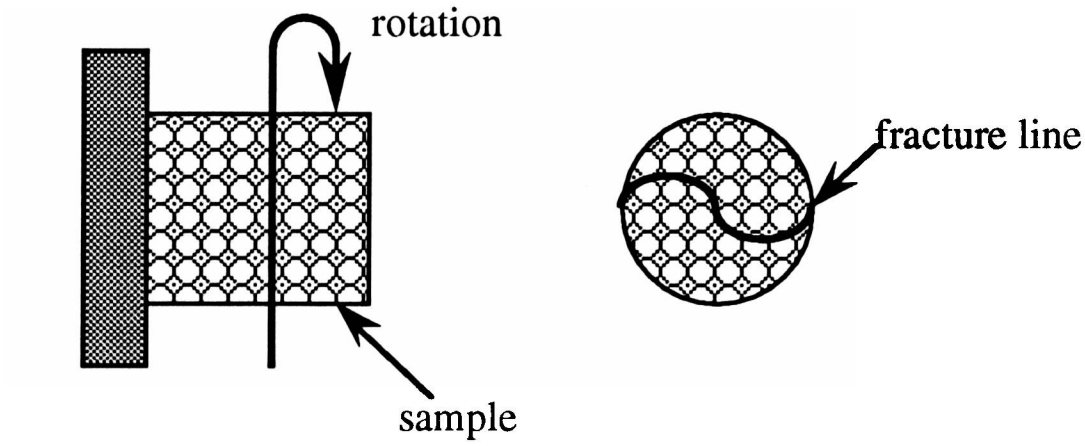


Figure 37: Fracture under an applied torsional stress[38]

5. Modulus of Elasticity

The modulus of elasticity is a measure of the capacity of a material to accomodate strains without becoming permanently deformed or fractured. It is an important parameter with regard to a ceramic, since the elasticity influences the ability of a material to withstand thermal shock. The elasticity constants of a material can be measured by any conventional method provided that a device for measuring the change in length of the test piece is incorporated into the appararus. Ceramic materials are usually tested using hydraulic apparatus fitted with accurate load cells and strain gauges, since the deflections to be measured will be very small.

When a bar of material is supported on knife-edges and subjected to a pressure, the length will be reduced or increased depending upon whether the load is tensile or compressive. Provided that the load has not been too great, the bar will return to its original dimensions once the pressure has been released. When a successively increasing load is applied and removed, the load which is just too great to permit the test piece to return to its original dimensions and results in bending, is taken as the elastic limit. The modulus of elasticity is then calculated using Equation 11, and is defined as the ratio of unit stress to unit strain at the elastic limit.

$$E = \frac{3\,l^2\,P}{4\,a^3\,b\,(t\,g\,\alpha)}$$ **Equation 11**

where E = modulus of elasticity
l = length
P = applied pressure
a = thickness
b = width
t g α = factor based on the angle of rise of one end of the bent test piece and on the length of the rising portion

6. Impact Tests

The resistance of a material to impact is a useful parameter to assess when the material is to be used in an application where rough handling is likely to occur or there is a possibility that the components will be struck against other objects or dropped. The tensile strength of materials is also used as an indication of resistance to impact, but is not always reliable in this respect.

One example of an impact test involves the use of a pendulum, at the end of which is a large flattened steel ball with a spherical striking surface. The sample to be tested is placed loosely against a wooden board and the pendulum is allowed to swing through a measured angle and strike the test piece. The blows are repeated, with the pendulum moving through greater angles, until the test piece fractures. The impact strength is then calculated by the formula:

$$E = W\,(\,1 - L\cos\theta)$$ **Equation 12**

where E = energy of impact
W = weight of the pendulum
L = length of the pendulum arm
θ = angle of swing

7. Hardness Testing

In some applications, the hardness of a material can be more significant than its ultimate strength. For example, in crushing and grinding applications the surface of the ore bodies tends to be abraded. Also there are aplications where the surfaces of materials are subjected to erosion by dusts, high velocity gas streams, molten slags and metals. Most methods of measuring hardness rely upon the observation of an indentation which is made in the surface of the test material subjected to an applied force. Others measure abrasion resistance or the amount of material removed by techniques which resemble milling, cutting or sand-blasting.

The simplest indentation test used is the Mohs' Hardness, where the surface of the sample is scratched in turn by a series of 'standard' materials which increase progressively in hardness. The hardness of the material is then quoted as that of the mineral which will just produce a positive indentation or scratch when viewed under a lens. The test must be used with discretion: crystal imperfections and crystallographic orientations often give false hardness values. Examples of the Mohs' Scale together with the typical series of minerals and convenient substitutes can be seen in Table 7.

Table 7: The Mohs' Scale[38]

Hardness Number	Material
1	Foliated talc
2	Rock salt or gypsum, or finger nail
3	Transparent calcite or copper wire
4	Fluorspar, scratches copper wire
4 - 5	Ductile iron; window glass
5	Transparent apatite
5 - 6	Blade of good pocket knife
6	Orthoclase felspar
6.5	File
7	Transparent Quartz
7 - 8	Will scratch a knife
8	Transparent topaz
9	Sapphire or corundum
10	Diamond

In Brinell hardness testing, the indentation is made in a polished specimen, by applying a static load to a hardened steel ball placed on the surface of the sample. The load is applied gradually and maintained for 15 seconds, the indentation is measured, and the Brinell Hardness Number (H) calculated using Equation 13. H is defined as the applied load divided by the spherical area of the indentation.

$$H(BHN) = \frac{P}{A} = \frac{P}{(\pi/2)\, D\, (D - \sqrt{(D - d^2)})} \qquad \textbf{Equation 13}$$

where H(BHN) = Brinell Hardness Number
P = load
A = area of indentation
D = diameter of indenter
d = mean diameter of the indentation

The Brinell method is widely used but very hard materials often indent the steel ball and invalidate the results. In the Vickers method the steel ball is replaced by a square based pyramidal diamond, the faces of which are at an angle of 136° to each other. The hardness number is calculated from the measurements of the square shaped indentation which appears in the sample surface (Equation 14).

$$H\,(VHN) = 1.854\ \frac{P}{d^2} \qquad \textbf{Equation 14}$$

where H(VHN) = Vickers Hardness Number
P = load
d = measured diagonal of the indent

Both the Vickers and Brinell methods involve measurement of the indentation under a microscope. In the Rockwell system a simpler method is employed and the indentation depth is measured on a dial gauge incorporated into the test machine. Two indenters are generally provided; a small steel ball operating at 100 kg for softer materials, and a conical diamond to be used for harder materials at 150 kg. A reference base point is determined at the commencement and conclusion of the test by applying a 10 kg load. The test gives results in terms of the deflection (in divisions) on a scale.

It is difficult to compare the hardness results of a material obtained by all of the hardness methods but a useful guide can be found in Table 8.

Table 8: A comparison of hardness values[38]

Vickers	Brinell	Rockwell C	Rockwell B	Mohs' Scale
+4000	-	-		10
2600	-			9
1600	940	82		8
1400	880	78		7
1200	810	73	-	
1000	740	68		
800	630	62		6
600	530	53	-	
400	390	41	114	5
200	200		93	4
100	100		58	3
50	50		27	2
25	25			
15	15		-	1

2.7: Common Casting Defects

2.7.1: Casting Bulge

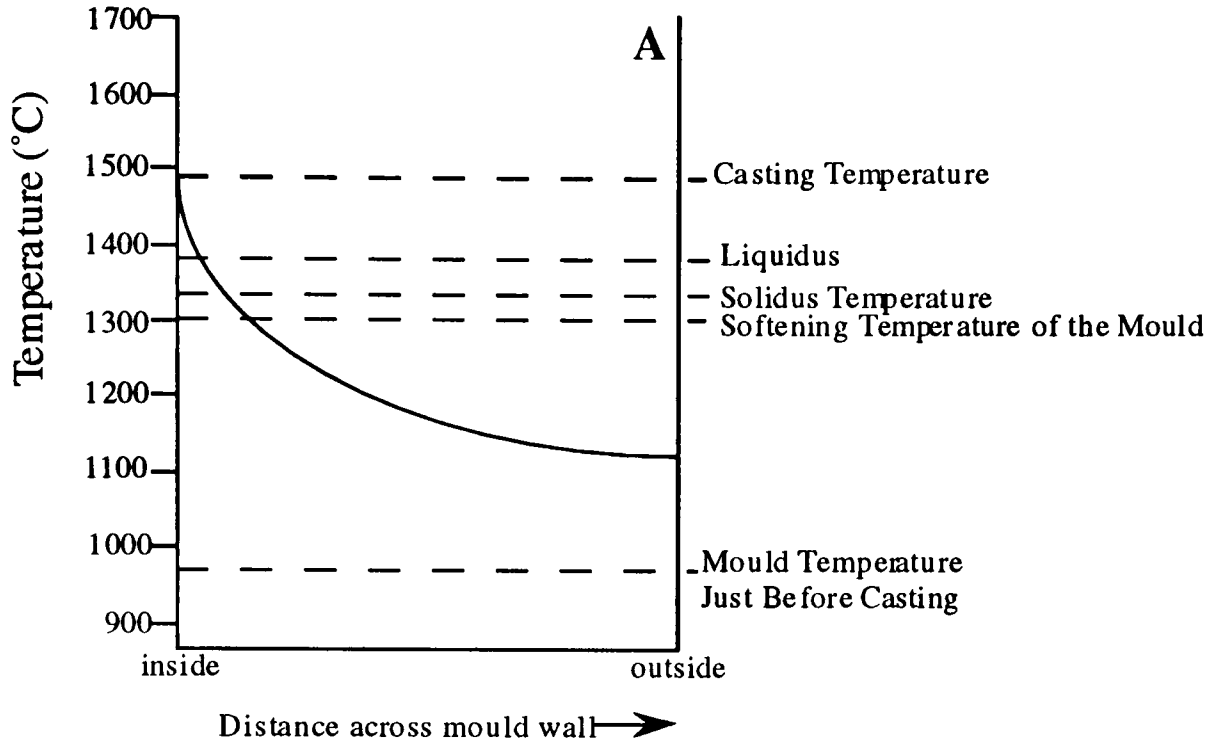
Casting flaws and defects are an unavoidable part of the investment casting process. Some problems, such as cracking and primary coat inclusions, can be directly related to deficiencies in mould manufacture. Cracking is usually caused by expansion of the wax during investing or during the dewaxing stage. Inclusions arise because of spalling within the primary coat or poor joints on the wax assembly which result in areas of 'flash' (excess material). Others, such as hot tears and shrinkage, are due to poor casting design. Most of these defects can be overcome by better design and more efficient mould production. However, the use of larger moulds has highlighted the problems of high temperature plastic distortion and cracking.

For many years foundries have periodically noted a major casting defect in both small and large components[96]. This defect involves large areas of external casting surface being convex instead of flat; a phenomenon commonly referred to as 'bulging'. This defect can be eliminated in smaller castings, but for larger castings the mould wall movement is more pronounced, with fractures and metal breakout occurring, making the problem more difficult to rectify.

Casting bulge is thought to result from mould wall movement after the pouring of the metal but before complete solidification of the casting[97]. This indicates that the mould wall cross-section is behaving plastically and distorting due to the elevated temperatures and high metallostatic pressures. Bulge is usually found on flat areas and is often associated with heavy section parts. A schematic illustration of the relative conditions under which plastic distortion will occur is shown in Figure 38.

Bulging can be alleviated by using thicker mould walls and lower mould temperatures before casting, and by providing mechanical and chilling support to the ceramic shell mould[96]. However, these modifications produce expensive moulds and do not cure the problem in all cases. Attention is now being focused on the role played by the binder, the gelling/drying conditions, shell thickness and the types of fillers being used. Research has shown[98] that the use of zircon as a refractory filler can reduce the extent of mould wall movement and that an inverse relationship exists between casting bulge and shell thickness. As such, thin shells show gross outward bulge but thick shells either remain flat or bulge inwards. Inward bulge can also lead to casting failure but is not considered as much of a problem since the extent can be controlled by decreasing the number of secondary coats.

Several theories concerning the cause of casting bulge are currently under investigation. These include high temperature creep of the silica binders[99], phase transformations within the binders and fillers[99], interactions between the binder and the refractory[97] and the low thermal conductivity and heat transfer of conventional shell formulations[97].



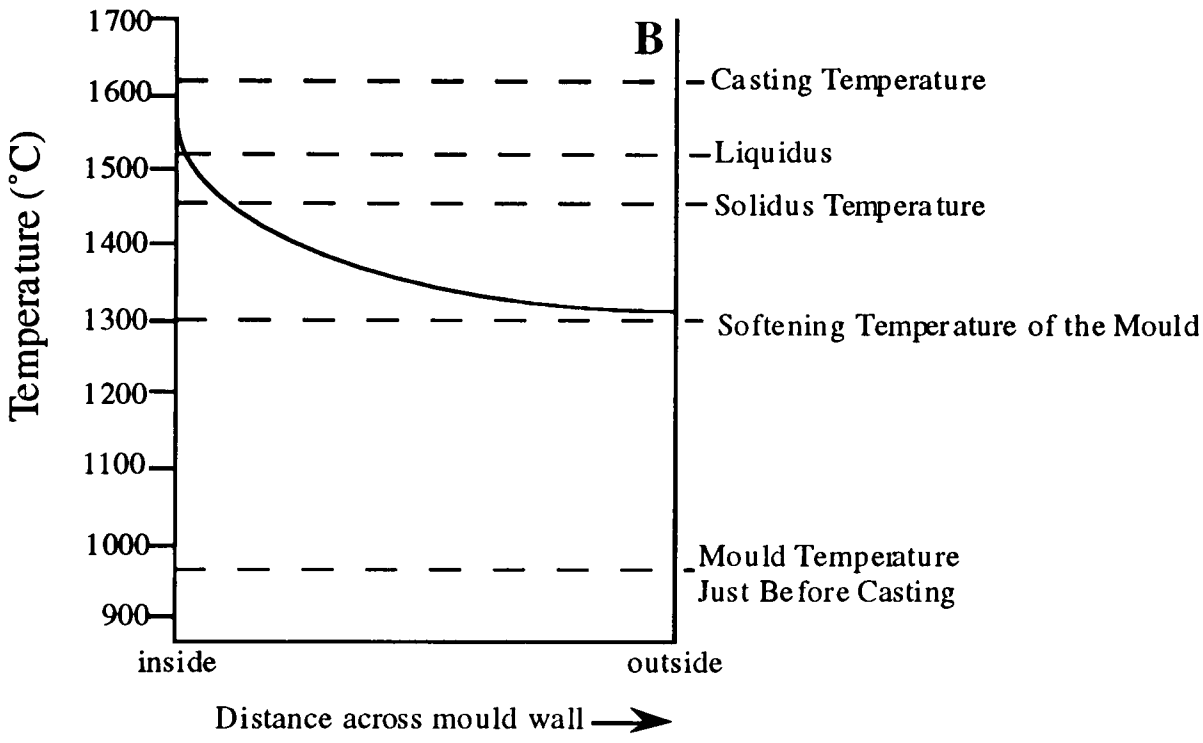


Figure 38: Schematic illustration of the relative conditions under which plastic distortion will occur in mould sections[96];

(A) Thin section of cast metal - smaller amount of heat transferred to mould before solidification of metal complete and removal of metallostatic pressure on mould - no distortion

(B) Thick section of metal cast - larger amount of heat transferred to mould raising the temperature of all mould wall thickness above its softening point before complete solidification of metal. Metallostatic pressure produces distortion if mould wall is not supported

2.7.2: Metal Mould Interaction

Many metals, when cast into a refractory mould, undergo a series of reactions with the ceramic which modify the metal surface. Interaction can occur through adherence of refractory materials to the metal or by the production of reaction layers which degrade and reduce the mechanical or corrosion properties of the metal close to the surface. It is vital, when producing an investment casting, to avoid this interaction. Surface integrity is a important parameter which makes the investment process attractive for the production of certain components such as turbine blades for the aerospace industry. Interaction may necessitate further surface finishing which is costly and undesirable. Metal mould interaction can also produce to non-metallic macro and micro inclusions in the castings which can seriously alter physical properties and lead to casting rejection[100].

Many non-specialised alloys are known to undergo extensive reaction with particular refractory systems. Silicate materials react with molten steel[101] causing wear of the refractory and the formation of reaction products that are carried into the steel as non-metallic inclusions. The interaction is the result of the reduction of silica by the manganese and carbon in the steel. The manganese oxide promotes the formation of glassy phases with silica, alumina and other oxides. These glassy phases have low melting points and as such are incorporated into the metal at the interface. This produces an increase in the silica content of the metal and a general weakening of the refractory structure leading to ceramic inclusions in the surface of the casting.

The presence of manganese in an alloy has a detrimental effect upon alumino-silicate and zirconia based refractories. Manganese reacts with oxygen in the atmosphere to form manganese oxide. This oxide then preferentially attacks silica containing refractories according to the reactions[102];

$$2\,MnO + SiO_2 = 2\,Mn_2SiO_4 \qquad \textbf{Equation 15}$$

$$MnO + SiO_2 = MnSiO_3 \qquad \textbf{Equation 16}$$

These crystalline phases both form liquid phases at low temperatures (1000° and 1150°C), which leads to erosion of the refractory. The reaction can be slowed by using very high purity zirconia or alumina refractories which withstand attack by manganese oxide. Elimination of oxygen using carbon, graphite or vacuum casting conditions has the same effect.

One of the most common causes of failure of alumina-silica refractories used in the steelmaking process is the reaction of the refractory with iron oxides at high temperatures[103]. Under the action of an oxygen partial pressure, FeO reacts with Al_2O_3 and SiO_2 to form a series of crystalline phases

such as cristobalite, tridymite, mullite, corundum, haematite, $Fe_2O_3.Al_2O_3$, spinel, iron cordierite, fayalite and wustite. This mixture of phases leads to the formation of low melting point oxides which become liquid and degrade the refractory.

Reactive metals such as titanium and its alloys are notoriously difficult to cast into ceramic moulds because of the extent of the interaction with the refractory material. Early attempts[104] to cast titanium into ordinary foundry moulds were unsuccessful due to the reduction of the silica, producing heavy reaction zones on the casting surface, oxide inclusions and a reaction layer called alpha-case. In order to reduce the reaction various systems have been investigated:

(1) The use of graphite moulds or carbonaceous primary layers[105].

(2) Tantalum, molybdenum, columbium, tungsten and thorium oxide non-reactive surfaces[106].

(3) The use of fluorides and oxyfluorides as constituents in the primary mould layers[107].

(4) Titanium enriched zirconium oxide and yttrium oxide crucibles[108].

(5) Moulds made from zirconium acetate bonded calcia-stabilised ZrO_2[109].

(6) The use of aqueous, acidic zirconia sol as a binder[110,111].

The casting of titanium into moulds having a very high ZrO_2 content on the surface produced low contamination of the surface such that the alpha-case layer was reduced to 0.05mm in depth[104]. Moulds having a major Y_2O_3 content in the mould surface (greater than 99%) showed an alpha-case less than 2.5×10^{-4} cm. However, though the interaction has been reduced, the alpha-case layer has not yet been completely eliminated.

'Spotted dick' or fusion spots are the foundry terms given to a casting defect which occurs primarily on the metal surface of high chromium steels. The effect is most commonly seen on 13% Cr steels, but a similar defect can be observed on 18/8 stainless steels. Fusion spots or pitting appears as a series of dark coloured, shallow depressions covering most of the area of the casting and especially on thicker metal sections. In addition to giving an irregular and unsightly surface, the slag pockets react with the metal surface giving rise to rapid corrosion[112]. The defect, if only slight, can be removed by various mechanical and chemical finishing methods, but more severe attacks degrade the metal surface to such an extent that complete removal cannot be carried out and the casting is scrapped.

The effect is believed to be caused by decarburization of the metal at the metal-mould interface which gives rise to the formation of carbon monoxide[113]. The CO bubbles then deform the surface of the casting and produce pitting depressions. Decarburisation is chemical and pitting a physical process. The presence of excess chromium, which is a carbide forming element, aggravates the condition due to the production of carbides which deposit as slags in the depressions.

Though the exact cause of the phenomenon is still under investigation, fusion spots are usually attributed to three main causes:

(1) Reaction between the carbon in the liquid metal and oxygen from the air trapped in the pores of the mould[113]

(2) Reaction between the carbon in the liquid metal and oxygen from the atmosphere[114]

(3) Reaction between the carbon in the liquid metal and the mould material, whereby the SiO_2 content is reduced[115]

Oxygen is required at the metal surface for the formation of the carbon monoxide. This can be obtained from within the pores of the mould or conveyed from the atmosphere through the ceramic shell to the interface. Carbon monoxide can also be obtained from the reaction of silica within the primary coat of the mould with carbon from the contacting metal. Research has also shown[101] that the defect is related to the solidification time of the casting. This rate is dependent upon the weight of the casting, the relative amount of surface available for heat emission and the capacity for heat absorption of the mould and its surroundings. Taking all these factors into consideration, the following preventative methods have been proposed and indeed do appear to reduce the occurrence of the defect[116]:

(1) Incorporate crushed graphite into the stucco or colloidal graphite into the back-up slurry

(2) Reduce mould temperature prior to casting

(3) Reduce casting temperature

(4) Inject a small quantity of halogenated hydrocarbon into the mould prior to casting

(5) Surround casting with a carbonaceous material

(6) Cast or cool in vacuum

(7) Use silica free mould materials

2.7.3: Hot Tearing

Hot tears or contractional stresses at elevated temperatures occur within the metal casting when there is a concentration of heat at a point ('hot-spot'). Accompanying the concentration of heat is a localised concentration of stress which, if it exceeds the strength of the metal, will form a tear. This appears as an intergranular crack which exhibits an oxidised fracture face. Shrinkage occurs because molten metal contracts as it cools. Listed below are several probable causes and suggested remedies which tend to be linked with the casting design[116]:

(1) Sharp internal angles - stresses can be reduced by the use of fillet radii.

(2) Incorrect design of the feeding system in which reservoirs of molten metal are badly placed leaving no surplus metal to fill the voids or internal shrinkage caused when the metal cools and contracts - to counteract this, reservoirs (feeders) are connected to the casting, to supply molten metal to the parts of the casting that solidify last.

(3) Restriction of casting contraction at higher temperature - alleviated by the use of lower strength moulds or by a reduction in the cooling rate.

(4) Major sectional changes in the casting - modify the casting design.

(5) Incorrect casting conditions - modify the casting conditions, e.g. increase mould temperature.

(6) Premature movement of the shell after casting - allow adequate time for complete solidification.

It is also believed that hot tearing is an intrinsic physical property of the metal itself and not just a function of the overall casting design. Tearing occurs at the site of defects, nucleated during turbulent flow of metal through the gating system [117]. For each metal there is a specific feed velocity above which turbulent flow occurs during feeding. As long as the velocity is held below this value then hot tearing should not occur. Thus, with careful design of the gates, it is believed that the defect can be eliminated from most castings.