	Metallurgical and Materials Engineering Laboratory II Experiment Booklet **MINERAL PROCESSING (ORE DRESSING)**

MINERAL PROCESSING (ORE DRESSING)

1. OBJECTIVE OF THE EXPERIMENT

In this experiment, it is aimed to investigate the crushing, grinding and separation steps according to the size of the ore preparation, the determination of the process parameters and also the flotation process which is one of the ore enrichment processes.

2. THEORETICAL INFORMATION

2.1 GENERAL TERMINOLOGY ON ORE DRESSING

Ore: The rock that is made up of one or more minerals, which are economically valuable and can be consumed directly or after some beneficiation operations, in industry. Ore is the raw material of metal production. If valuable minerals do not contain metallic elements, it is called industrial raw material instead of ore dressing.

Mineral: A mineral is a naturally formed solid and inorganically crystallized structure that has a homogeneous, specific chemical composition and a specific crystal structure.

Concentrate: It is a product obtained by beneficiation of minerals which are formed as a result of ore dressing or beneficiation processes and which are aimed to be separated from raw ore.

Tenor: Percentage of metal or economically valuable minerals in an ore.

2.2 ORE DRESSING AND BENEFICIATION

The process of raising the percentage of the base metal mineral in the low grade ore occurring in nature. By taking advantage of the different properties of the gangue minerals and the base metal mineral, minerals are partially separated from each other by ore dressing or beneficiation process.

Ore dressing is applied due to economic and technological reasons.

a) Technological Reasons for Ore Dressing

Some ores need to provide certain conditions (grain size, grade and element content) in order to be technologically produced. Examples of these conditions are given below.

Example 1. For quartz sand in glass making; 0.1 mm < Grain Size < 0.5 mm and % Fe_2O_3 < 0.05% are required.

Example 2. For iron ore used in pig iron production; 10 mm < Grain Size < 100 mm is required. For this purpose, crushing, grinding and sintering-pelletizing is applied. In addition, both % P and % $Na_2O + K_2O$ must be < 0.1%.

Example 3. In order to produce calcined magnesite or sinter magnesite at high quality from magnesite ore: SiO_2 < 0.5 % and 2 mm < Grain Size < 30 mm are required.

b) Economic Reasons for Ore Dressing

There are basically two reasons:

a) Using an uneconomic ore directly as is produced from the quarries (eg, producing lead metal directly from a 5 % Pb-containing ore) is never economical. With the ore dressing process, the lead percentage is increased to 60% and economic efficiency is ensured.

b) To further increase the economics of an economic ore as produced from the quarries.

For example, it is economical to produce pig iron directly from a 50 % Fe-containing ore, but increasing the iron tenor to over 50 % further increases the economics.

2.2.1 ORE DRESSING PROCESSES

Crushing: It is the coarse size reduction carried out with the help of crushers. It is applied in two stages; coarse crushing (average 100 mm grain size) and fine crushing (1-10 mm grain size).

GRINDING: It is the fine size reduction carried out with the help of mills (below 0,1 mm grain size).

SCREENING: It is the dimensioning done with the help of screens.

SEPARATION BY SIZE: Minerals are separated from each other partially by using density, magnetic, electrical and surface properties.

2.2.1.1 CRUSHING

Crushing is the first step of size reduction. It is conducted to make one of the different minerals freed from others, the process is done with the aim of providing suitable size or surface area or suitable size for the purpose of use.

The forces applied in the field; impact, compression or crushing, cutting and friction forces. The devices used for crushing are called crushers. They are mechanical tools that apply pressure, impact and shear force to the grain to bring them to a smaller grain size.

Crushing machines are developed especially in terms of design features such as product characteristics, machine costs and energy use. Thus ore dressing machines in a variety of shapes, structures and sizes are used.

Crushing is applied to grain sizes between 200 and 0.5 cm. Crushing between 200-10 cm is named coarse crushing; and crushing between 10-0.5 cm, it is called fine crushing. Jaw, cone and hammer crushers are the most widely used types of crushers in ore dressing plants.

Removal of the crushed material in the desired size from the crushing cycles or classification of the material according to the size; different sieves are used according to the applied process, structure of the ore, size, physical and chemical properties. These are classified as; according to the structure of the sieve surface sheet, parallel bar screens, and wire mesh;; according to their working stationary (fixed grid and stationary arched sieve) and moving (traveling grate, rotary screen, shaking screens and vibrating screens).

2.2.1.2 GRINDING

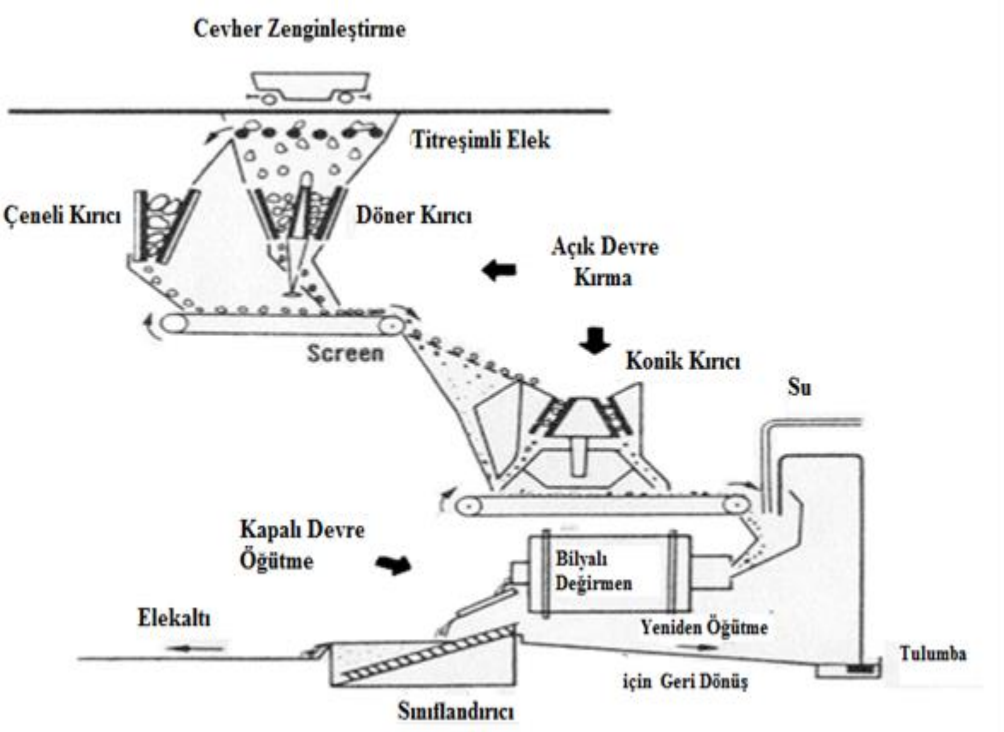
Grinding is the final stage of size reduction after crushing. The process is conducted with the aim of freeing one of the various minerals from others in the ore, providing suitable size or surface area or requested size for the purpose of use. The forces applied in grinding are; impact, compression or crushing, cutting and friction forces.

The devices used for grinding are called mills. The mills are selected according to the type of the ore, size of the desired product in the grinding cycles or after grinding. **Ball and rod mills** are the most commonly used in ore dressing plants. Grinding is carried out as wet or dry depending on the flow of the process and the state of the ore. According to the grinding scheme, the classifier and other process machines in the system are selected. Dry grinding requires about 1.3 times more power than wet grinding. For removal from grinding circuits or classification according to the size of the material; different classifiers are used according to the applied process, structure of the ore, size, physical and chemical properties. These are known as; hydrocyclones, mechanical classifiers (spiral classifiers, notched classifiers, solid centrifugal classifiers) and air classifiers.

2.2.1.3 SCREENING

Screening is the process of separating a solid material mixture into components of different dimensions using screens. According to the screen size used in the sieving classifying "mesh number" concept is used. Mesh number indicates the number of holes per unit area (in^2 or mm^2) of a screen.

By sieving, two types of products are obtained, one screen underflow (subsieve) and oversize (oversieve). Industrial sieves are divided into two main divisions: "fixed sieves" and "moving sieves", depending on whether the surface of the workpiece is fixed or movable. The simplest forms of fixed screens are grids. Grids are the most suitable type for large sized items. They are usually made oblique and allow the pieces falling from the grid spacing to separate from the grid as the material on them moves down. various motions are given to the grid to reduce clogging in the moving screen. With these movements, material is pushed in one direction and sieving is facilitated.



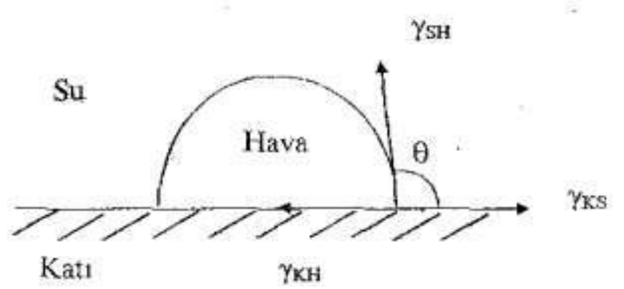
Cevher zenginleştimenin açık devre ve kapalı devre işlemlerinin bölümleri

2.2.2 FLOTATION

Flotation is derived from the word float. In the ore beneficiation processes, flotation is a method of separating some minerals in an ore from other minerals sunk in the water by floating and removing some of them from the water. In this process, the separation is made by using the differences in the surface properties of the minerals.

Wetting of particles is known to be one of the important parameters affecting many technological processes such as wetting, flotation, agglomeration, solid-liquid separation and dust suppression. In the flotation system consisting of solid, liquid and gas phases, if the solid phase prefers the gas phase relative to the liquid, it is called hydrophobic, if liquid phase is preferred to gas phase, it is called hydrophilic. Hydrophobic minerals are low surface-energy minerals (coal, graphite, sulfur, talc, etc.). The wettability / hydrophobicity and buoyancy properties of the solids were investigated in terms of solid-water and solid-water vapor interfaces, chemical bonds, bulk properties, crystal structure of the solids and reactivity of the solids with water.

The high contact angle (θ) in the solid, liquid and air triple system means that the wetting of the liquid by the liquid is minimal. The forces in the solid, liquid, air triple system are as shown in Figure 2. The case where the triple phase is balanced is expressed by Young Equation.



Young Eşitliği: $\gamma_{KS} = \gamma_{KH} + \gamma_{SH}\cos\theta$

$$\cos\theta = \gamma_{KS} - \gamma_{KH} / \gamma_{SH}$$

Figure 2. The forces in solid, liquid, air triple system and Young Equation

It is possible to determine the wetting and buoyancy characteristics of minerals or associations by several methods, empirical and empirical. The numerical value parameter obtained from these techniques is the critical wetting surface tension, γ_c. At low liquid surface stresses lower than this γc, the mineral loses its hydrophobicity or buoyancy property by being completely wetted by this solution. The surface tension (γ_{SH}) of the liquid used for a good contact angle (between solid-liquid-air interfaces), ie θ> 0, must be greater than the γ_c value of the mineral. This is the first of the conditions required for the successful flotation.

Low surface energetic minerals (γc <72 dyn / cm) are wetted by surface-energized fluids lower than the Critical Wetting Surface Energy (γc). Selective separation of the two layers in the flotation system is based on whether one of the solids is partially wetted by the flotation solution or completely wetted by the solution while the other layer is not wetted (θ = 0 state). Partially wetted solids clinging to the floating air bubbles.

Two of the most commonly used techniques for measuring the hydrophobicity of minerals or solids, and therefore the wetting of the γC value that determines good flotation, are the "contact angle measurement method" and the "flotation method".

Application areas of flotation for ore dressing are;

- Flotation of metallic ores
- Flotation of non-metallic ores
- Cleaning of solid fuels

The advantages of flotation are;

- Beneficiation of very fine grained ores
- Beneficiation of complex ores
- Control of the product tenor as desired
- Insignificance of specific weight difference of minerals.

The disadvantages of flotation are;

- High costs compared to gravity and magnetic separation methods
- Because of the excessive grinding of the ore, sometimes the loss of metal is high and the grinding costs increase
- Causing environmental pollution

2.2.2.1. Reagents Used in Flotation

Various reagents are added to the flotation medium in order to float or suppress the desired mineral(s) in the flotation. It is possible to sort these reagents as follows.

Collectors: It is a chemical substance that imparts hydrophobicity to surfaces by modifying surface properties through adsorbing to the surfaces of mineral(s).

Frothers: These are foam forming chemicals in flotation circuits. The main goal of the foaming agents is to be able to form a foam of sufficient volume and strength. Foams should be able to explode easily after exiting the flotation cell.

Control Reagents: reagents that are used to adjust the flotation conditions.

i) Suppressor Reagents: These are the flotation reagents are used to suppress unwanted mineral(s). These reagents reduce collector adsorption on the mineral surface.

ii) Activating Reagents: Reagents that increase collector adsorption to the surface of mineral(s).

iii) Other Control Reagents: Reagents in this group provide; regulation water hardness, bind the harmful ions for the flotation, flocculation or dispersion of some minerals in the pulp.

2.2.2.2. Flotation Machines

Flotation machines are usually composed of successive cells. the residue of previous cells is subjected to flotation in each cell. There is a connection between each cell, or a residual flow plate between cells. Air inlet and mixing operations to the pulp inside the cell are conducted by three types of methods;

- Self- aeratied mechanical cell (Agitation)
- Air blown mechanically agitated cells (Sub-aeration)
- Air blown, air mixed cell (Pneumatic)

These properties are taken into consideration for the construction of various types of cells.

Currently the most used cell types in the industry are self- aerated mechanical cell types manufactured by companies such as Denver, Fagergren, Humbold, Massco.

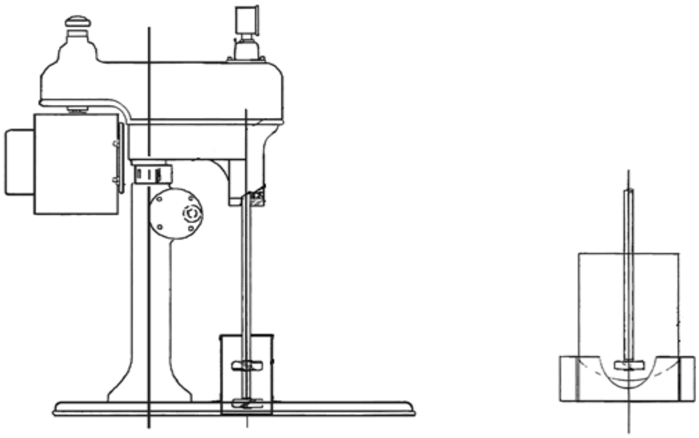


Figure 3. Denver flotation machine

3. EQUIPMENT AND MATERIALS

- Various Crushers and Mills
- Sieves and Screening Device
- Denver Flotation Machine
- Pipet, Washing Bottle, Enamel Containers
- Precise Balance
- Reagents (Collector, Frother)
- Ground Galena Ore

4. EXPERIMENTAL PROCEDURE

4.1 Ore Dressing Experiment

- ✓ The weight of the mixture to be examined for particle size distribution is weighed and recorded. The weighed mixture is fed to the crusher and crushing is performed by operating the crusher. After the crushed particles are removed from the crusher, they are weighed again and recorded.
- ✓ The sieves are arranged on the sieving device in the order of their interval, according to their mesh numbers. Then the crushed ore at the top of the sieve set is fed.
- ✓ The screws of the sieve set are squeezed and sieving is carried out by operating the device for ten minutes.
- ✓ By taking the sieve set from the machine, the amount of material left in each sieve and the total amount of sieved material are recorded in Table 1.1.

4.2 Flotation Experiment

- ✓ 200 g. of galena ore with -200 μm grain size is weighed and adjusted to 20% solids ratio depending on the volume of flotation cell. The cell is placed in the flotation machine and the pulp is mixed by starting the machine. The pulp is conditioned by stirring for 5 minutes.

- ✓ 1-2 drop of the appropriate collector used for galena ore, is added to the pulp and mixing is continued for 5 minutes.

- ✓ One drop of the frother, which provides for the formation of an aerosol foam for floatation of the hydrophobicized minerals, is added. After the addition of frother the pulp is conditioned for another 1-2 mins.

- ✓ After the end of the last conditioning period, the air inlet tap of the flotation device is opened and the pulp is aerated. Mineral(s), whose surface has become hydrophobic, adhere to the air bubble and accumulate on the surface as foam. Foams are removed from the surface and concentrated in a separate container, and the process is terminated after the extent of the mineral to be floated has finished.

5. ASSIGNMENTS

1. Write the objective and procedure of the experiment.
2. The results of each sieve analysis shall be recorded in the chart given in Table 1.1.

Table 1.1 Sieve analysis data and calculations

Sieve Dimension (mm)	Weight		Cumulative Oversieve %	Cumulative Subsieve %
	g	%		
Total				

3. By using the sieve analyzes obtained from the experimental procedure, sieve analysis charts of the input and output products will be formed and total subsieve and oversieve curves will be drawn.

4. Determine the average grain size from the intersection of the two drawn lines.

5. Find the theoretical average grain size by the formula given below and compare the theoretical grain sizes found at the intersection of the straight lines.

$$\text{Theoretical Average Grain Size} = \frac{\sum(X.M)}{100}$$

X= Sieve interval or diameter (same as grain size), M=% grain class weight

6. The beneficiation ratio will be determined by weighing concentrate and residue after flotation. (Z = Ore Fed / Concentrate).

6. REFERENCES

[1] Yiğit E., Cevher Hazırlama I, II ders notları, ZKÜ Yayını

[2] KAYTAZ Y., "Cevher Hazırlama", İTÜ Maden Fakültesi, 1990

[3] ERGUNALP F. "Cevher hazırlama prensipleri" , İTÜ Yayınları, 1959

[4] Zeki ÇİZMECİOĞLU, Üretim Metalürjisi Prensipleri Ders Notları, YTÜ, 2008

BIOCERAMIC SCAFFOLD PRODUCTION

1. OBJECTIVE

The aim of this experiment is to learn the production of 3-dimensional ceramic-based tissue scaffolds for use in ceramic materials and hard tissue applications.

2. LITERATURE

Tissues in the human body have the ability to regenerate themselves thanks to a certain cycle of construction and destruction. However, this cycle may be disrupted due to reasons such as age factor, trauma, and disease. When remodeling system breaks down, the bone tissue cannot repair itself and thus loses its functions.

There are various methods that can be used to support bone regeneration and restore bone restoring properties, in situations that decrease quality of life. One of them is the use of "tissue scaffolds". The purpose of this application is to restore bone loss by remodelling lost bone tissue. In these applications, biocompatible synthetic or natural materials are used.

2.1 BONE STRUCTURE

Bone is a well-organized natural composite structure from macro level to nano level (Figure 1). The main component of the organic part of the bone is collagen (polymer) and the main component of the inorganic part is the hydroxyapatite (ceramic) mineral. The two most important bone types are cortical and cancellous bone. Cortical bone (Figure 2) is a dense structure with high mechanical strength and is also known as compact bone. Spongy or trabecular bone (Figure 2) is a porous structure located at the ends of long bones such as femur or short bones within the boundaries of the cortical bone [1].

Cortical bone forms the hard, stiff and dense cortex layer that supports the whole body. It has an outer layer called the “Periosteum” and an inner layer called the “Endosteum”. The Osteon/Havers system is the functional unit of the cortical bone. It consists of haversian canals the center surrounding the blood vessels and the haversian canal is surrounded by coaxial lamella layers. The bone matrix (thin layers called lamellae, 3-7 μm width) is formed by bone-forming cells called osteoblasts. Osteoblasts are formed by the differentiation of the mesenchyme stem cells (MSC) of the bone marrow. The remodeling process is initiated by osteoclasts responsible for the absorption of the bone matrix [2].

2.2 BONE REPAIRING BIOMATERIALS

Bone plays an important role in the homeostasis (balancing) of minerals. The most important of these minerals, phosphate and calcium ions are stored in the bone and can be released into the blood when necessary. Another important function of bones is movement, load bearing and protection of the internal organs of the body. Bone tissue is a dynamic and highly vascularized tissue. Most fractures do not require any surgical intervention. However, surgical operation is required for large bone defects and non-union fractures. The high regenerative feature of bone is a process that continues throughout the life of the individual. Treatment of damaged tissues can be carried out using an autograft or an allograft. Autografts, which are accepted as the gold standard, are structures that are taken from the person and implanted into the damaged tissue. The bone graft taken from the person itself integrates into the body faster and reduces the risk of contamination. On the other hand; Autografts have several disadvantages due to blood loss, longer surgical time, infection and limited amount of graft material.

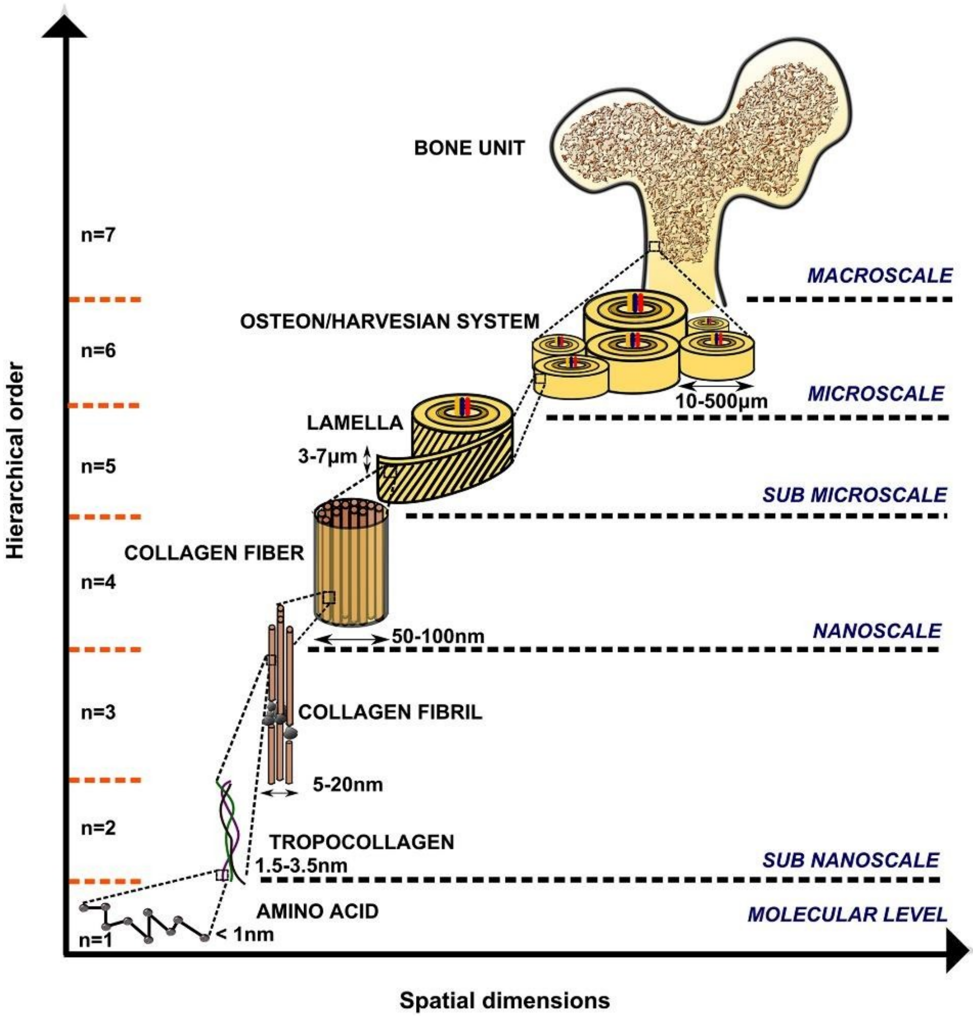


Figure 1 Hierarchical arrangement of bone in various length sizes [2]

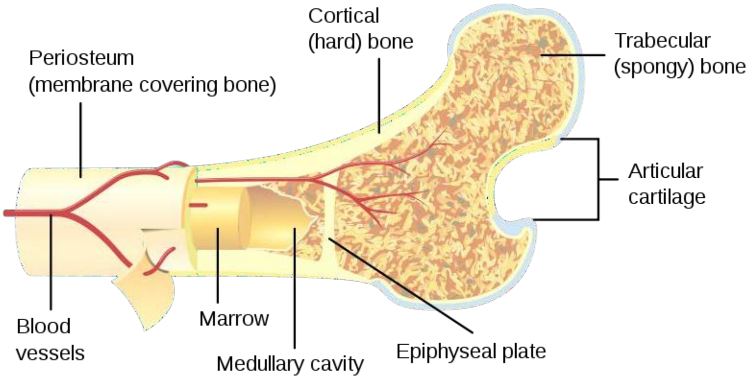


Figure 2 Cross section of bone [3]

Allogenic bone grafts are structures that are implanted from another person.These structures should provide osteoinductivity and osseointegration. Osteoinductivity means that the bone can grow. In osteoinductive grafts, spongy bone formation occurs towards the graft surface, pores, channels or pipes. Osseointegration is about the attachment between bone and implant. Appropriate placement of a graft is affected by many factors, such as the type of graft and the site of placement.

There are also various synthetic grafts developed in place of biological grafts. In the past, researchers was focused on the development of bioinert materials, while today they focuses on the development of bioactive materials that can bond with biological molecules. Materials that can be used in place of autologous and allogenic grafts can be listed as bioactive ceramics, bioactive glasses, biological or synthetic polymers and composites. In these materials, it is easier to avoid transplant problems such as infection or poor compliance with environmental stresses. The ideal material is expected to be completely replaced by biological tissue.

The term tissue scaffold is used for three-dimensional (3D) biomaterials, which provide a favorable environment for cells to regenerate tissues and organs. The purpose of the production of tissue scaffolds is to ensure that regenerative signals are sent to the cells to naturally simulate the tissue healing. The most important fenomenon in tissue scaffolds are their 3D structures. Interconnected pores and high porosity allow 3D tissue regeneration, cell growth, cell proliferation and differentiation, and the diffusion of waste and decomposition products. The pore size should be large enough to allow cells to move, but small enough to allow cells to attach to the scaffold. Decomposition of the scaffold should take as long as tissue regeneration. Therefore, an ideal scaffold for bone tissue should be osteoconductive, biodegradable and have appropriate mechanical properties.

2.2.1 Types of Materials

Historically, the main feature expected from first-generation biomaterials is biocompatibility, while the feature expected from second-generation biomaterials is bio-interaction. Third generation biomaterials are expected to be bio-reactive, for example, they should activate genes, proliferation and differentiation of cells. Today, the most commonly used materials for bone tissue scaffold production are inorganic materials and natural or synthetic polymers.

Polysaccharides (such as starch, alginate, chitin/chitosan, hyaluronic acid derivatives) or proteins (such as soy, collagen, fibrin gels, silk) help cell adhesion and function. However, immunogenicity may occur due to pathogenic impurities, moreover controlling of the mechanical properties and biodegradation may be more difficult.

Synthetic polymers such as poly (lactic acid) (PLA) and poly (glycolic acid) (PGA) and their copolymers are widely used because of their superior mechanical properties and decomposition rates in cell transplantation and in scaffolds for tissue engineering.

Metals can be considered as the oldest type of material used in implant production. The first metals used in biomaterial applications were aluminum, lead, gold and silver. Today, titanium and its alloys are the most commonly used metallic biomaterials for dental and orthopedic implants due to their high biocompatibility, low toxicity and high corrosion resistance.

Inorganic materials such as metals, bioactive glasses, tricalcium phosphate (TCP), hydroxyapatite (HA) and their combinations are other groups of materials used in bone tissue engineering due to their similarity to the bone mineral phase. There are also biphasic ceramic structures such as HA-TCP and wollastonite developed from these materials. Bioceramics are biomaterials used not only in bone tissue engineering, but also in orthopedics and dentistry. The most widely used bioceramics in bone tissue engineering are HA, TCP and their composites [4].

2.3 SCAFFOLD PRODUCTION TECHNIQUES

2.3.1 Conventional Production Methods

Conventional methods for fabricating porous tissue scaffolds mainly include methods such as solvent casting/particulate leaching method, microsphere sintering, gas foaming process, sponge (replica) method, melt molding method, phase separation method, fiber bonding method and electrospining.

2.3.1.1 Solvent Casting and Particulate Leaching

Solvent casting/particulate leaching method is the most used method in tissue scaffold production. In this method water-soluble particles are added to the polymer solution, and the mixture is cast into the desired shape. After the solvent is removed (evaporated or lyophilized), the resulting structure is treated with water to remove porogen particles, and then porous structure is obtained. In addition to salt and sugar, lipids are also used as porogen particles. When using this method, the pore size and porosity of the tissue scaffold can be controlled by adjusting the added porogen size and the particle / polymer ratio. However, the shape of the pores is limited to the shape of the porogen. The most important advantage of the method is the use of a small amount of polymer. Although it is easy to apply, it is not possible to obtain thin membranes and very fine 3-dimensional porous structures in the thick structures since it is difficult to remove the particles with water. The high amount of solvents, some of which may be toxic, and the presence of residues of these solvents in the structures can prevent cell adhesion and proliferation [5].

2.3.1.2 Gas Foaming

Porous ceramic scaffolds can also be produced using the gas foaming technique. Ceramic sludge can be foamed by the following methods;

- Passing air bubbles through the mud,
- Sweeping air into the mud using high speed rotary blades,

Stabilizing agents such as agar or polymeric materials are used to keep the sludge stable. Porous tissue scaffolds can also be obtained by pouring and drying the ceramic slurry and then burning the drying structure. In sintering, stabilizing organic agents leave a porous ceramic structure and move away from the structure. With this method, it is possible to manufacture ceramics with pores connected with each other [6].

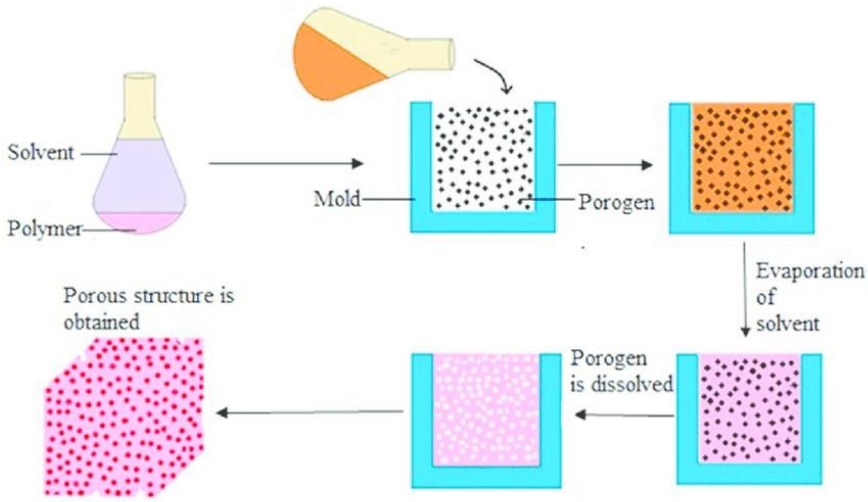


Figure 3 Schematic representation of the solvent casting /particulate leaching method [7]

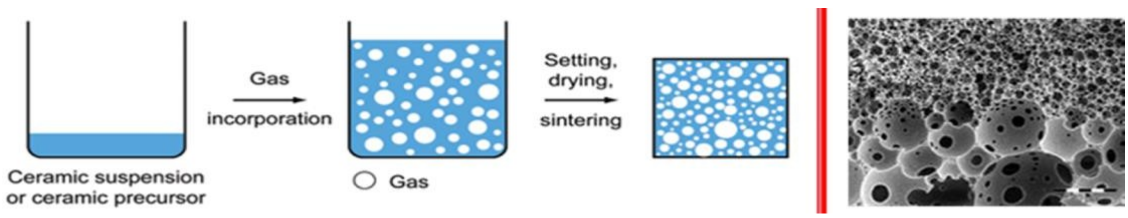


Figure 4 Schematic illustration of the gas foaming method [8]

2.3.1.3 Replica (Sponge) Method

Polymeric foam substrates can also be used to produce porous ceramic materials. The ceramic mud is either absorbed into the foam or covered with foam ceramic slurry and allowed to dry before burning. During the sintering process the polymeric particles burn and ceramic is sintered to crystalline structure which is contained interconnected pores.

Ceramic density and pore size, shape and distribution depend on the method used. Open porous structures with up to 70% porosity can be produced by taking a positive view of the foam. In this method, the mud is coated on the foam strips and during the combustion, the foam is made open porous and burns. The positive image of the porous foam is given in Figure 5 (a). Alternatively, the foam can be absorbed completely with ceramic slurry so that all voids are filled. A negative image of the foam is obtained during combustion as shown in Figure 5 (b). In this way, the material will have approximately 5-10% porosity.

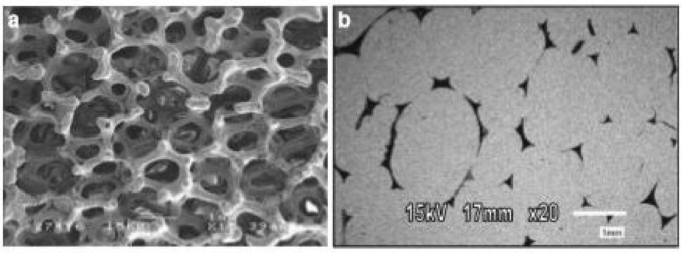


Figure 5 (a) Open porous HA structure (b) Dense HA ceramic structure with interconnected porosity [6]

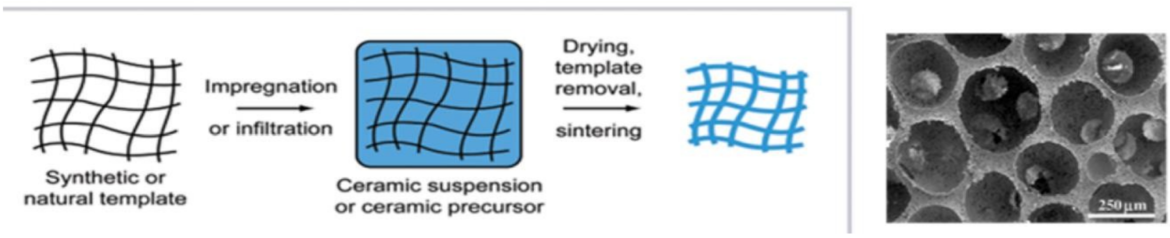
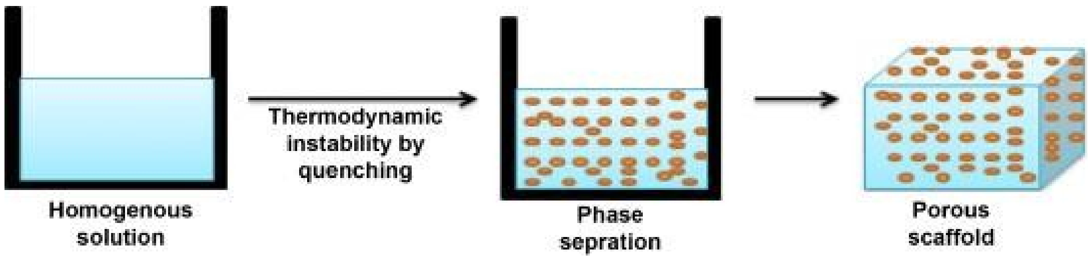


Figure 6 Schematic representation of the replica method [8]

2.3.1.4 Phase Separation Method

In this method, multicomponent systems such as polymer-water emulsions are used. These systems can become thermodynamically unstable at certain temperatures and phase separation occurs when the free energy decrease. First, two polymer-rich and polymer-poor phases are formed. Then, by removing the solvent (by lyophilisation or solvent extraction), the polymer-rich phase solidifies and the porous structure is obtained. Phase separation can be done in two ways: thermal separation (TIPS) and solvent and phase separation (SIPS). In the more commonly used SIPS method, the polymer solution is placed in a container and placed in a bath where the polymer is insoluble but has a second solvent that can form a solution with the polymer solvent. Phase separation occurs by contact of solvents. The structure of the tissue scaffold can be controlled by adjusting the phase separation conditions. The phase separation method can be in the form of solid-liquid phase separation and liquid-liquid phase separation. In the solid-liquid phase separation method, by lowering the temperature of the polymer solution, the solvent crystallizes, and by separating the solvent crystals (sublimation or solvent exchange) pores are formed in the regions where the solvent crystals are separated. In the liquid-liquid phase separation method, polymer-rich and polymer-poor phases are separated by bringing the polymer solution to a temperature above the critical solution temperature. Open porous structures are formed by separating the solvent. Phase separation method is also used in the preparation of internally linked nanostructures. Phase separation is a simple method, but there are disadvantages such as limited solvent combinations, requiring additional steps for washing, and solvent residues in the prepared structure [5]. Compared with the solvent casting/particle separation method, it is possible to obtain structures with a lower pore diameter and higher pore area by freeze drying method. The formation of closed pores in structures prepared using this method is the most important disadvantage of the method.



Şekil 7 Schematic representation of the phase separation and lyophilization method [9]

2.3.1.5 Fiber Bonding

Fiber bonding method is one of the oldest tissue scaffolding production methods and developed for the purpose of using biodegradable polyglycolic acid (PGA) surgical threads as tissue scaffolds. Briefly, a solution of poly-L-lactic acid (PLLA) dissolved in a solvent that does not dissolve PGA is added to the network prepared from PGA. After removing the solvent, the PLLA-PGA composite structure is heated to above the melting temperature of the PGA. Thus, the PGA strands that are in contact with each other melt and physically merge. The PLLA in the structure is again removed by using solvent. Following the drying process, a tissue scaffold consisting of PGA, with structural integrity is obtained [5].

2.3.1.6 Electrospining

The electrospinning method is based on the principle of obtaining polymers in fiber structure using electrostatic forces. In this method, high voltage is applied to the polymer solution in a capillary feeding unit. When the formed electrostatic forces overcome the surface tension of the polymer solution, the flow formed in the form of a fiber jet is collected in an unstable structure in a fiber form on a conductive plate or roller acting as a collector. Electrospinning method is important in tissue engineering applications since it can be applied to many polymers. By using the electrospinning method, it is possible to obtain non-knitted mesh or linear structure fibers from nanometer sizes to micron sizes under different process conditions. Many parameters affect the properties of the product to be obtained, such as the properties of the polymer and the type of solvent, the flow rate of the solution, the applied voltage, the distance of the needle from the collector, and the polymer concentration. In the structures obtained by this method, fiber size is the most important factor as it affects the pore size and porosity of the scaffold. However, it is not a suitable method for obtaining three-dimensional structures, since only thin membranes can be prepared by the electrospinning method [5].

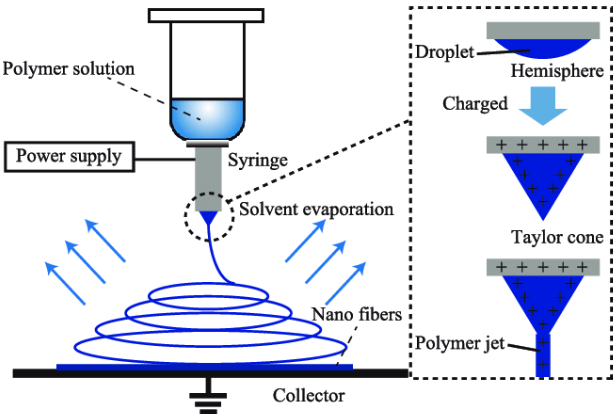


Figure 8 Schematic representation of the electrospinning method [10]

2.3.1.7 Melt Molding

The melt molding method was developed to overcome restrictions in the solvent casting/particulate leaching method. In this method, the polymer is heated to temperatures above the glass transition temperature, the particles that will act as porogen are mixed and pressed under constant pressure. Washing with water is carried out to remove particles from the mold. Thus, a porous structure is formed. In this method, organic solvents are not used and tissue scaffolds can be produced as desired by changing the mold. However, the melt molding method can only be applied to thermoplastic polymers [5].

2.3.2 Rapid Prototyping

Rapid prototyping methods are tissue scaffold manufacturing methods based on advanced computer technology. 3D printing, stereolithography (SLA), fused deposition method (FDM) and selective laser sintering (SLS) methods are rapid prototyping methods. In these methods, the design of complex shaped structures is formed using software such as computer aided design (CAD), computed tomography (CT) and magnetic resonance imaging (MRI). The prepared digital information is converted into special section format as layer series for the device. Tissue scaffolding is produced by spreading binders between polymer layers processed using original devices [5]. These methods are successfully applied for scaffold production with controlled pore structure and shape [1].

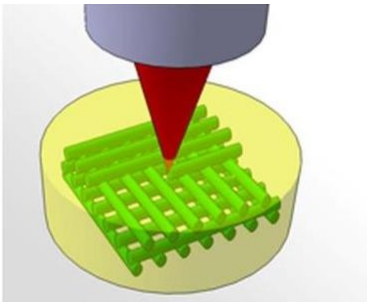


Figure 9 Schematic representation of scaffold production with FDM [11]

3. MATERIALS AND DEVICES USED IN THE EXPERIMENT

- Glass and Other Materials: Beaker, Glass Stirring Rod, Spatula, Graduated Cylinder, Sample Weighing Container, Burette, Filtering Flask, Filter paper

- Devices: Magnetic Stirer, pH Meter, Analytical Balance, Oven, Sintering Furnace

- Chemicals: $Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4$, HCl, NH_4OH, Porogen (Starch), Binder (Triethyl phosphate), Distilled water

4. METHODS

4.1 SYNTHESIS OF HYDROXYAPATITE CERAMICS

In the first step of the bone scaffold production hydroxyapatite will be synthesized.

$$\mathbf{10\ Ca(NO_3)_2.4H_2O\ +\ 6\ (NH4)_2HPO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2}$$

- 1M calcium nitrate tetrahydrate [$Ca(NO_3)_2.4H_2O$] and 1.2M diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] are dissolved separately in 1L and 0.5L distilled water, respectively.
- The Ca-containing solution is added to the P-containing solution with an addition rate of 4 m /min.
- The pH of the solution is adjusted to 9 with ammonia [NH_4OH].
- The solution is mixed for 1h and then aged at 37 °C for 24h.
- Aged ceramic sludge is filtered with blue band filter paper and washed with distilled water.
- Sludge dried at 80 °C and then sintered at 900 °C for 1 h and finaly ground in agat mortar.

4.2 PREPERATION OF CERAMIC SLURRY

- A suspension is prepared by mixing 11 g of the grounded hydroxyapatite ceramics with 25 mL of distilled water.
- In a separate place, 6 mL of triethyl phosphate and 0.4 g of starch are mixed with the appropriate amount of distilled water until dissolution occurs. If no dissolution occurs, the solution is heated.
- After obtaining a homogeneous mixture, methyl cellulose + triethyl phosphate is added to the hydroxyapatite slurry, which is mixed under control.
- The mud is mixed for 24 hours to obtain stabilization.

4.3 PREPARATION OF TISSUE SCAFFOLDS BY THE REPLICA METHOD

- Sponges to be used for impregnation are cut as 1*1*1 cm.
- Sponges are immersed in ceramic mud and waited until they absorb the mud. Then excess of the sludge is removed by air spraying.
- Ceramic-impregnated sponges are first dried at 60-80°C. Then sintering process is carried out as follows;
  (a) Samples are heated to 300°C in 1 h and kept at this temperature for 1 h,
  (b) Then the temperature is increased to 1200°C in 5°C/min intervals and kept at this temperature for 5 h to produce bioceramic scaffolds.

5. ASSIGNMENT

Prepare a report containing your observations and experimental results in all steps of the ceramic tissue scaffolding production experiment. Provide information on the types of grafts and scaffold production methods in the literature section of the report.

6. REFERENCES

[1] J.R. Jones, L.L. Hench, Regeneration of trabecular bone using porous ceramics, Curr. Opin. Solid State Mater. Sci. 7 (2003) 301–307. doi:10.1016/J.COSSMS.2003.09.012.

[2] S. Sankar, C.S. Sharma, S.N. Rath, S. Ramakrishna, Electrospun nanofibres to mimic natural hierarchical structure of tissues: application in musculoskeletal regeneration, J. Tissue Eng. Regen. Med. 12 (2018) e604–e619. doi:10.1002/term.2335.

[3] No Title, (n.d.). https://en.wikipedia.org/wiki/Bone.

[4] P. Chocholata, V. Kulda, V. Babuska, Fabrication of scaffolds for bone-tissue regeneration, Materials (Basel). 12 (2019) 568.

[5] A.Y. ARİKAN, A.T.D. KARAKEÇİLİ, Doku iskelelerinin süperkritik karbondioksit ortamında hazırlanması ve karakterizasyonu, Ankara Üniversitesi Fen Bilimleri Enstitüsü Kimya Mühendisliği Anabilim Dalı, n.d.

[6] R. Narayan, Biomedical materials, Springer Science & Business Media, 2009.

[7] U.G. Sampath, Y.C. Ching, C.H. Chuah, J.J. Sabariah, P.-C. Lin, Fabrication of porous materials from natural/synthetic biopolymers and their composites, Materials (Basel). 9 (2016) 991.

[8] I.J. Kim, J.G. Park, Y.H. Han, S.Y. Kim, J.F. Shackelford, I.J. Kim, J.G. Park, Y.H. Han, S.Y. Kim, J.F. Shackelford, Wet Foam Stability from Colloidal Suspension to Porous Ceramics: A Review, J. Korean Ceram. Soc. 56 (2019) 211–232.

[9] D. Rana, G. Ratheesh, S. Ramakrishna, M. Ramalingam, Nanofiber composites in cartilage tissue engineering, Nanofiber Compos. Biomed. Appl. (2017) 325–344. doi:10.1016/B978-0- 08-100173-8.00013-2.

[10] S. Maeda, T. Kato, H. Kogure, N. Hosoya, Rapid response of thermo-sensitive hydrogels with porous structures, Appl. Phys. Lett. 106 (2015) 171909.

[11] A.S. Çakmak, Biyofiziksel ve Biyokimyasal Uyaranlarla Desteklenmiş Doku İskeleleri ile Mezenkimal Kök Hücrelerin Osteojenik Farklılaşmasının İncelenmesi, Fen Bilimleri Enstitüsü, 2014.

DEPT. METALLURGICAL AND MATERIALS ENGINEERING
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METALLOGRAPHY AND MICROSTRUCTURE

METALLOGRAPHY & MICROSTRUCTURE

OBJECTIVE:

1. To learn and to gain experience in the preparation of metallographic specimens.
2. To examine and analyze the microstructures of metals and metallic alloys.

MATERIALS AND EQUIPMENT:

Grinders, polishing wheels, drying fans, and metallurgical microscopes. Acrylic resin etching solutions (nitric acid, alcohol), Al_2O_3 (5µm, 1µm and 0.05 µm) and consumable supplies as needed and given engineering alloy specimens.

THEORETICAL BACKGROUND:

Metallography is essentially the study of the structural characteristics or constitution of a metal or an alloy in relation to its physical and mechanical properties. The most important part of metallography deals with the microscopic examination of a prepared metal specimen. Correct preparation begins with the selection of a suitable specimen and continues to the etching stage where the structure of the specimen is revealed. The microscopic examination then defines clearly such structural characteristics as grain size, the size, shape and distribution of secondary phases and non-metallic inclusions; and segregation and other heterogeneous conditions.

These characteristics profoundly influence the mechanical properties and physical behavior of the metal. Metallographic examination can provide quantitative information about specimen grain sizes, amount of interfacial area per unit volume, and the amount and distribution of phases. When these and other constitutional features are determined by microscopic examination and the extent to which they exist in the microstructure is known, it is then possible to predict with considerable accuracy the expected behavior of the metal when used for a specific purpose. Of equal importance is the fact that, within limits, the microstructure can provide an accurate picture of the mechanical and thermal treatments that a metal has received.

Preparation of Specimens

The technique for preparing metal sections can be divided into two groups, those processes involving the use of emery papers and coarse abrasives (grinding) and the subsequent operations using fine abrasives (polishing treatments). Grinding must be carried out carefully in such a way that all microscopic constituents in the surface are preserved and that the grinding medium is not embedded in the sample. To achieve this, the specimen is ground on successively finer grades of emery (sand) paper. During grinding, the specimen is held with the newly formed scratches at right angles to the scratches introduced on the preceding paper. Undue pressure should be avoided since the disturbed layer this produces on the surface can extend to considerable depth. For some heat treated alloys and in particular for many of the soft metals, it is an advantage to use paper thoroughly wetted. Grinding also removes surface deformations. After grinding, the specimen is washed thoroughly in water and then polished. Mechanical polishing can best be carried out by holding the specimen against a rotating disc covered with a suitable pad that is impregnated with either a suspension of polishing alumina in water or diamond dust oil.

Mounting of Specimens

It is frequently convenient to mount small specimens in bakelite or acrylic to aid specimen preparation, grinding, polishing and etching. The basic idea is that bakelite powder is thermosetting. Therefore the specimen is placed in a tube 2/3 filled with powder. The tube is heated while the powder is compressed. The pressure and heat are removed when the powder has completely melted and the bakelite has set. To maintain orientation small shot are sometimes placed next to the specimen in some identifying arrangement.

Fig. 1: A Hot Mounting Press

Although inferior in quality to compression-type molding, cold molding (room temperature) is often used with epoxy to mount samples by simply mixing the epoxy and pouring it over a sample that is positioned facedown in a cold-mounting ring. When the epoxy cures the specimen can be prepared. Caution must be exercised when cold mounting due to relatively poor adhesion between the specimen edges and the epoxy plug; gaps often form which can degrade the quality of the specimen.

Fig. 2: Various resins used for cold mounting

Grinding and Polishing Procedure

The following instructions indicate the general method to be used in specimen preparation. The edges of cylindrical metal specimens must first be beveled off to avoid damaging the polishing cloths. For Mg and Al and their alloys, use the aluminum polishing wheels.

Stage	Abrasive	Lubricant	Cloth
Rough Grinding	Silicon Carbide	Tap Water	
Fine Grinding	**Grit 240**		
	Grit 320		
	Grit 400		
	Grit 600		
Rough Polishing	Gamma **Alumina 1.0µ**	Tap Water	Rayon
Final Polishing	Gamma **Alumina 0.05µ**	Tap Water	Rayon

Fig. 3: An Automatic Polishing Machine with Two Rotating Discs

It is important that abrasive is not carried from one part of a sequence to another. Therefore, you must wash both the specimens and your hands between each step. When grinding the specimens, they are rubbed forward in one direction until the surface is completely ground, that is, until only grinding marks due to the particular paper can be seen on the whole surface. For soft metals, further grinding for a short time is advisable after this condition is reached to remove any sub-surface deformation produced in previous operations. The direction of grinding is changed from paper to paper so that the removal of previous grinding marks is easily observed. Polishing is carried out on cloth covered rotating wheels. During the polishing, the specimen should be held firmly in contact with the polishing wheel, undue pressure should be avoided. During polishing, the specimen should be rotated or moved around the wheel to give an even polish. The specimens must be washed and dried before both polishing steps.

Etching

Etching is done to bring out the structure of the polished specimen. It is usually performed by subjecting the polished surface to the chemical action of an appropriate reagent. However, the polished specimen should first be examined unetched. Inclusions, flaws, scratches and other defects can be observed in this way, and if they are identified before etching, subsequent confusion and misinterpretation can be largely avoided. The specimen to be etched is treated by immersion in, or by swabbing with, the appropriate reagent. It is impossible to lay down general rules for the time of etching. Usually the desired effect will be produced between ten seconds and two minutes. The specimen after etching should be washed in a stream of running water. The surface should be dried untouched by holding in air current. When selecting etching times, it is more desirable to under-etch than to over-etch. If a specimen, after a first attempt is found to be insufficiently etched, the etching process can usually be repeated without further preparation of the surface. A specimen that is over-etched can only be corrected by repolishing and then reetching for a shorter time.

Nital, a Nitric Acid - Alcohol mixture, is the etchant commonly utilized with common irons and steels. Nital is dripped onto the specimen using an eye-dropper or cotton swab. Ten seconds to one minute is usually sufficient for proper etching depending on sample and nital concentration. The sample is immediately washed under running water, rinsed with alcohol and dried in an air blast. Do not touch, wipe or swab the specimen following etching; dry off the rinsing alcohol on the specimen with the air blast and then move on to the microscopic examination stage!

Table 1: Etchants used for different materials

Materials	Composition	Application Procedure
Iron & Steel	1-5 Parts Nitric Acid 100 Parts Alcohol	Immerse/Swab
Copper & Brass	1 Part Ammonium Hydroxide 1 Part 3% Hydrogen Peroxide 1 Part Water	Swab
	5 g Ferric Chloride, 10 ml Hydrocloric Acid 100 ml Water	Immerse
Aluminum	5-10 g Ammonium Persulphate 1 ml Hydrofluoric Acid 99 ml Water	Immerse
	10 g Sodium Hydroxide, 100 ml Water	Immerse
Stainless Steels	10 g Oxalic Acid 100 ml Water	Use Electrolytically
	5 ml Sulfuric Acid 100 ml Water	Use Electrolytically

Microscopic Examination

Initial microscopic viewing should be done utilizing a stereo microscope, which reveals a three-dimensional scanning of the specimen surface. The specimen is placed on the stage of the microscope so that its surface is perpendicular to the optical axis.

Fig. 4: Stereo Microscope

Detailed viewing is done with a Metallurgical Microscope. A metallurgical microscope has a system of lenses (objectives and eyepiece) so that different magnifications (25X to 1000X) can be achieved. The important characteristics of the microscope are: (1) magnification, (2) resolution and (3) flatness of field. The resultant magnification is the product of the magnifying power of the objective and that of the ocular. Scanning Electron Microscopes (SEMs) are capable of magnifications up to 20,000X and Transmission Electron Microscopes (TEMs) are utilized to view at magnifications up to 100,000X for highly detailed microstructural study.

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Fig. 5: Metallurgical Microscope

The Metallurgical Microscope

A metallurgical microscope differs from a biological microscope in the manner by which the specimen is illuminated. Because of the inability of visible radiation to propagate through a metal specimen, observations are made using light reflected from the polished surface. A horizontal beam of light is deflected by a plane glass reflector, upward and through a microscope objective onto the surface of the specimen. A certain amount of incident light will be reflected from the specimen surface back through the objective lens system and then through a second lens system, the microscope eyepiece.

The total visual magnification obtained by the combination of a given eyepiece and objective is equal to the product of the magnifications of the two systems. These magnifications are usually marked clearly on the appropriate parts. When examining a metallographic specimen, the objective of lowest magnifying power should first be used. Subsequently, greater detail of particular areas can be obtained by using progressively higher magnifications. The different objectives are mounted on a rotating head, so that their focal planes are very nearly at the same level. After focusing at the lowest magnification, only small adjustments should be necessary at higher magnifications.

Grain Size Determination

In single phase specimens, the ASTM grain size of the metal can be estimated by comparing the image at 100X with standard microstructure examples corresponding to standard grain sizes from 1 to 10. Also, suitable eyepieces etched with a square 0.01" x 0.01" in size can be used to calculate the number of grains per square inch, N.

The ASTM grain size number, n, can be calculated using the following relationship:

$$\mathbf{N\ (M/100)^2 = 2^{(n-1)}}$$

N = number of grains per square inch at 100X
n = ASTM grain size number
M = Magnification

For single phase materials, ASTM grain size number is given to denote the grain sizes. These are not the actual grain size values, but the latter can be derived from the ASTM grain size number, **n**; the larger the grain size number, the smaller the grains. If there are **N** grains per square inch at a magnification M then there are $(N)^{1/2}$ grains along a 1 inch length. The size of each grain at magnification M is then $1/(N)^{1/2}$ inches.

The actual size of the grain is given by Actual **Grain Size =** $\mathbf{1/(N\ M)^{1/2}}$

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METALLOGRAPHY AND MICROSTRUCTURE

EXPERIMENTAL STUDY:
Please be careful while using the equipment in the lab. Switch off all equipment and tidy the lab before you leave.

Using steel, aluminum and/or brass (60% Cu; 40% Zn) specimen, and the metallurgical microscope, analyze the microstructure of your given engineering alloys. Identify the phase or phases present and the grain size of the material from your metallographic examination. Study the microstructures using the metallurgical microscope and appropriate phase diagrams. Provide interpretation of your microstructures and prepare a laboratory report of your experiment.

Metallography Observation Record

Grind, polish, and etch the specimens given to you. Draw the microstructure you observe in your specimen.

Magnification:
Specimen:
Etchant:
Observation:

Stage I: Making Specimen Mounts:

Cold mounting procedure will be used to mount the specimens. Place the sample in a mounting cup with the help of mounting clips and then pour a mixture of resin mixture of two components). Now allow the resin to solidify (curing) and then take the sample out of the mounting cup. Applying release agent to the walls of the mounting cup before pouring the resin will help in easily removing the sample after curing process.

Stage II: Grinding

The specimens will be taken and grinded on different emery papers (SiC) using grinding machine.

Procedure:

(1) Open water line located behind grinder.

(2) Starting on the 120 and then 240 grit size, place prepared specimen, or metal face down of abrasive surface, and being sliding specimen against abrasive in a forward and backward motion.

(3) Next, turn specimen 90 degrees and repeat above procedure on the 320 Grit surface.

(4) Again turn specimen 90 degrees and repeat procedure (2) now on the 400 Grit surface.

(5) Finally, turning specimen 90 degrees and repeat procedure (2) now on the 600 Grit surface.

(6) Close water line.

Stage III: Polishing Wheels

Polish the specimen on polishing wheels using liquid suspension of Al_2O_3 and water, which is a very fine abrasive, until a mirror like finish is obtained. Start with 5µm and then with 1 µm and then proceed to 0.05 µm grit size Al_2O_3 powder polishing station. At this stage the microscopic examination may reveal cracks, seams, non-metallic inclusions, and any other similar scale inhomogeneties.

Stage IV: Etching the Surface

Etching is the selective attack by a chemical reagent that reveals the microstructural detail of the polished mount. The grain boundaries are attacked to a higher extent than grains because of their high energy. This results in depression of grain boundaries. To reveal the crystalline structure of the specimen, the polished surface is etched using appropriate etching solution. For this experiment use 3% Nitol (97%Alcohol-3% Nitric Acid) to etch the surface of the polished steel specimen. For brass specimens 50% nitric acid solution can be used. The etching solution may be applied on the specimen using a swab. It is very important to not over etch or under etch the specimen.

Stage V: Microscopy

The etched specimen will be examined using metallurgical microscope. The digital image of the grain structure will be saved for further image analysis.

REFERENCES

- ASM Handbook, Metallography and Techniques
- Material Science and Engineering- An introduction by W. D. Callister
- Engineering Metallurgy- Part I by R. A. Higgins
- Materials Science and Engg. By V. Raghavan
- Manufacturing Engineering and Technology by S. Kalpakjian

BINARY PHASE SYSTEMS

1. OBJECTIVE OF THE EXPERIMENT

The aims of binary phase system is to understand the thermodynamic principles behind free-energy curves, how free-energy curves relate to equilibrium phase diagrams and be able to construct a binary phase diagram from cooling curves

2. THEORETICAL INFORMATION

2.1 INTRODUCTION

The phase diagram is a crucial part of metallurgy - it shows the equilibrium states of a mixture, so that given a temperature and composition, it is possible to calculate which phases will be formed, and in what quantities. As such it is very valuable to be able to construct a phase diagram and know how to use it to predict behaviour of materials.

The main theory behind phase diagrams is based around the latent heat that is evolved when a mixture is cooled, and changes phase. This means that by plotting graphs of temperature against time for a variety of different compositions, it should be possible to see at what temperatures the different phases form.

It is relatively easy to produce a rough binary phase diagram, but although it is quick to take readings for the top part of a phase diagram, it takes longer, and hence more sensitive equipment to monitor the changes that take place when a solid changes phase. A typical simple binary phase diagram is shown in Fig.1.

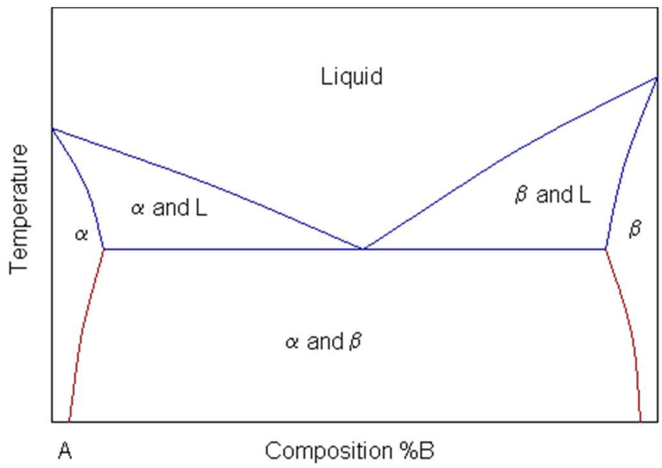

Figure 1 Schematic illustration of a typical simple binary phase diagram.

Where L stands for liquid, and A and B are the two components and α and β are two solid phases rich in A and B respectively. The blue lines represent the liquidus and solidus lines, which are relatively simple to measure. The red lines involve a solid-to-solid transition, and so require much more sensitive equipment.

However, there is also a lot of thermodynamic theory behind phase diagrams, which allows more problematic or more complex systems to be predicted, and this can lead to faster creation of phase diagrams, as it can take a long time to pick up all the stable phases in experiments, and there is not always the time available for such practical work.

A crucial point to remember is that a phase diagram should always display the equilibrium phases, and so with cooler temperatures, these are hard to attain due to kinetic problems. Even at higher temperatures, there may be problems of having enough time for the solid to fully equilibrate as the system is cooling.

2.2 THERMODYNAMICS: BASIC TERMS

2.2.1 Internal Energy, U

The internal energy of a system is the sum of the potential energy and the kinetic energy. For many applications it is necessary to consider a small change in the internal energy, *dU*, of a system.

$$dU = dq + dw = CdT - PdV = TdS - PdV \quad (1)$$

Where *dq is* the heat supplied to a system, *dw is* the work performed on the system, *C* is the heat capacity, *dT* is the change in temperature, *P* is the pressure and *dV* is the change in volume. At constant volume,

$dU = C_V dT$

2.2.2 Enthalpy, H

Enthalpy is the constant pressure version of the internal energy. Enthalpy,

$H = U + PV$

Therefore, for small changes in enthalpy,

$$dH = TdS + VdP \quad (2)$$

At constant pressure, $dP = 0$, thus

$dH_p = C_P dT$

2.2.3 Entropy, S

Entropy is a measure of the disorder of a system. In terms of molecular disorder, the entropy consists of the configurational disorder (the arrangement of different atoms over identical sites) and the thermal vibrations of the atoms about their mean positions. A change in entropy is defined as,

$$dS > \frac{dq}{T} \quad (3)$$

- For reversible changes, i.e. changes under equilibrium conditions, $dq < TdS$
- For natural changes, i.e. under non-equilibrium conditions, $dq = TdS$

2.2.4 Gibbs free energy, G

The Gibbs free energy can be used to define the equilibrium state of a system. It considers only the properties of the system and not the properties of its surroundings. It can be thought of as the energy which is available in the system to do useful work.

Free energy, *G*, is defined as,

$G = H - TS = U + PV - TS$

For small changes,

$$dG = -SdT + VdP \quad (4)$$

For changes occurring at constant pressure and temperature,

$dG = -SdT$

Therefore,

- $dG = 0$ for reversible (equilibrium) changes,
- $dG < 0$ for non-reversible changes.

From this it is clear that *G* tends to a minimum at equilibrium.

2.3 THERMODYNAMICS OF SOLUTIONS

Consider a mechanical mixture of two phases, A and B. If this is then transformed into a single solution phase with A and B atoms distributed randomly over the atomic sites, then there will be,

- An enthalpy change associated with interactions between the A and B atoms, ΔH_{mix}
- An entropy change, ΔS_{mix}, associated with the random mixing of the atoms
- A free energy of mixing,

$$\Delta G_{mix} = \Delta H_{mix} - \Delta S_{mix} \quad (5)$$

Assume that the system consists of N atoms: $x_A N$ of **A** and $x_B N$ of **B**, where, x_A = fraction of **A** atoms and $x_B = 1 - x_A$ fraction of **B** atoms

2.3.1 Enthalpy of mixing

In calculating ΔH_{mix} it is assumed that only the potential energy term undergoes any significant change during mixing. This change arises from the interactions between nearest-neighbour atoms. Consider an alloy consisting of atoms A and B. If the atoms prefer like neighbours, A atoms will tend to cluster and likewise B atoms, so a greater number of A-A and B-B bonds will form. If the atoms prefer unlike neighbours a greater number of A-B bonds will form. If there is no preference A and B atoms will be randomly distributed.

Let

w_{AA} be the interaction energy between A - A nearest neighbours,

w_{BB} that for B - B nearest neighbours and

w_{AB} that for A - B nearest neighbours.

All of these energies are negative, as the zero in potential energy is for infinite separation between atoms.

Let each atom of A and B have co-ordination number ***z***.

Therefore, the total number of nearest-neighbour pairs is ***Nz*/2**.

Probability of A - A neighbours = X_A^2

Probability of B - B neighbours = X_B^2

Probability of A - B neighbours = $2X_A X_B$

For a solid solution the total interaction energy is,

$$H_s - U_s = \frac{zN}{2}\left(X_A^2 w_A + X_b^2 w_B + 2X_A X_B w_{AB}\right)$$

For pure A, $H_A = \frac{zN}{2} w_{AA}$

For pure B, $H_B = \frac{zN}{2} w_{BB}$

Hence the enthalpy of mixing is given by,

$$\Delta H_{mix} = \frac{zN}{2} X_A X_B \left(2w_{AB} - \left(w_{AA} + w_{BB}\right)\right) \tag{6}$$

We can define an interaction parameter

$$W = \frac{zN}{2} \left(2w_{AB} - \left(w_{AA} + w_{BB}\right)\right)$$

Therefore,

$$\Delta H_{mix} = W\, X_A X_B \tag{7}$$

- If A-A and B-B interactions are energetically more favourable than A-B interactions then $W > 0$. So, $\Delta H_{mix} > 0$ and there is a tendency for the solution to form A-rich and B-rich regions.
- If A-B interactions are energetically more favourable than A-A and B-B interactions, $W < 0$, $\Delta H_{mix} < 0$, and there is a tendency to form ordered structures or intermediate compounds.
- Finally if the solution is ideal and all interactions are energetically equivalent, then $W = 0$ and $\Delta H_{mix} = 0$.

2.3.2 Entropy of mixing

Per mole of sites, this is

$$\Delta S_{mix} = -kN\left(X_A \ln X_A + X_B \ln X_B\right) = -R\left(X_A \ln X_A + X_B \ln X_B\right) \tag{8}$$

(the derivation of this result makes use of Stirling's approximation) where N = Avogadro's number, and $kN = R$, the gas constant. A graph of ΔS_{mix} versus x_A has a different form from ΔH_{mix}. The curve has an infinite gradient at $x_A = 0$ and $x_A = 1$.

The free energy of mixing is now given by,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = W\, X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right) \tag{9}$$

- For $W < 0$, ΔG_{mix} is negative at all temperatures, and mixing is exothermic.
- For $W > 0$, ΔH_{mix} is positive and mixing is endothermic.

2.4 FREE ENERGY CURVES

For any phase the free energy, G, is dependent on the temperature, pressure and composition.

2.4.1 Pure Substances

For pure substances the composition does not vary and there is little dependence on pressure. Therefore the free energy varies greatest with temperature.

The phase with the lowest free energy at a given temperature will be the most stable. The curves for the free energies of the liquid and solid phases of a substance have been plotted in Figure 2. It shows that below the melting temperature the solid phase is most stable, and above this temperature the liquid phase is stable. At the melting temperature, where the two curves cross, the solid and liquid phases are in equilibrium.

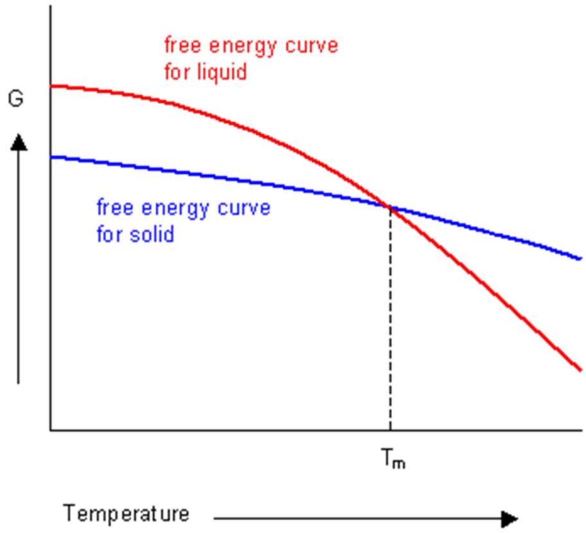

Figure 2 Difference in free energy between liquid and solid close to the

2.4.2 Solutions

Solutions contain more than one component and in these situations the free energy of the solution will become dependent on its composition as well as the temperature. It is shown above that the free energy of mixing is:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = W\ X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right) \quad (9)$$

The shape of the ΔG_{mix} curve is dependent on temperature. For the curve shown in Fig.3 the value of ΔH_{mix} is positive, leading to a maximum on the curve at low temperatures. ΔG_{mix} is always negative for low solute concentrations as the gradient of ΔS_{mix} is infinite at $x_A = 0$ and $x_A = 1$.

At high temperatures there is a complete solution and the curve has a single minimum. At low temperatures the curve has a maximum and two minima. In the composition range between the two minima (denoted by the dashed lines) a mixture of two phases is more stable than a single-phase solution.

The free energy of a regular solid solution, ΔG_{sol}, is the sum of the free energy of mixing ΔG_{mix} and the free energy of fusion ΔG_{fus} and it is expressed as

$$\Delta G_{solution} = \Delta G_{mix} + \Delta G_{fusion} \quad (11)$$

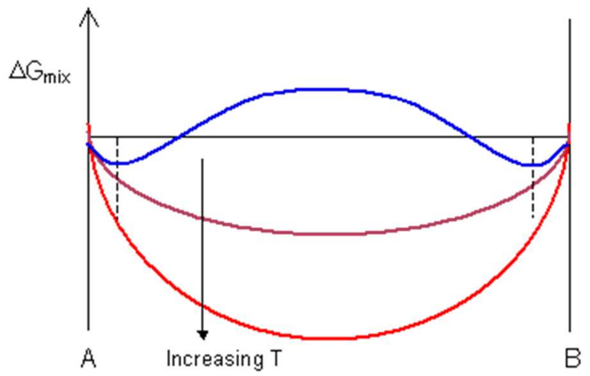

Figure 3 The effect of ΔH_{mix} and T on ΔG_{mix}.

2.4.3 Free energy of fusion

When a liquid solidifies there is a change in the free energy of freezing, as the atoms move closer together and form a crystalline solid. For a pure component, this can be empirically calculated using Richard's Rule:

$$\Delta G_{fusion} = -9.5\,(T_m - T) \qquad (10)$$

where T_m is the melting temperature and T is the current temperature.

- $\Delta G_{fusion} = 0$ at the melting temperature of the component.
- $\Delta G_{fusion} < 0$ below the melting temperature of the component.
- $\Delta G_{fusion} > 0$ above the melting temperature of the component.

2.5 PHASE DIAGRAMS

2.5.1 A Simple Phase Diagram

Free energy curves can be used to determine the most stable state for a system, i.e. the phase or phase mixture with the lowest free energy for a given temperature and composition. A schematic free-energy curve for the solid phase of an alloy is shown in Figure 4. The solid shown could either exist as a mixture or as a homogeneous solution of A and B. The figures 4 and 5 show that an alloy of composition C can exist in different configurations with differing free energies. In the figure 4 the free energy of unmixed A and B is shown as the diagonal black line. The free energy of this mixture at composition C is shown as a red point.

For most systems there will be more than one phase and associated free-energy curve to consider. At a given temperature the most stable phase for a system can vary with composition. While the system could consist entirely of the phase which is most stable at a given composition and temperature, if the free energy curves for the two phases cross, the most stable configuration may be a mixture of two phases with compositions differing from that of the overall system.

The total free energy of the system in any given two-phase configuration can be found by linking the two phases in question with a straight line on a free-energy plot. Taking a line that is a common tangent to the two free-energy curves produces the lowest possible free energy for the system as a whole. Where the line meets the free energy curves defines the composition of each phase. For positions where it is not possible to draw a common tangent between the two free-energy curves the system will sit entirely in the phase with the lowest free energy. The borders between the single- and two-phase regions mark the positions of the solidus and liquidus on the phase diagram

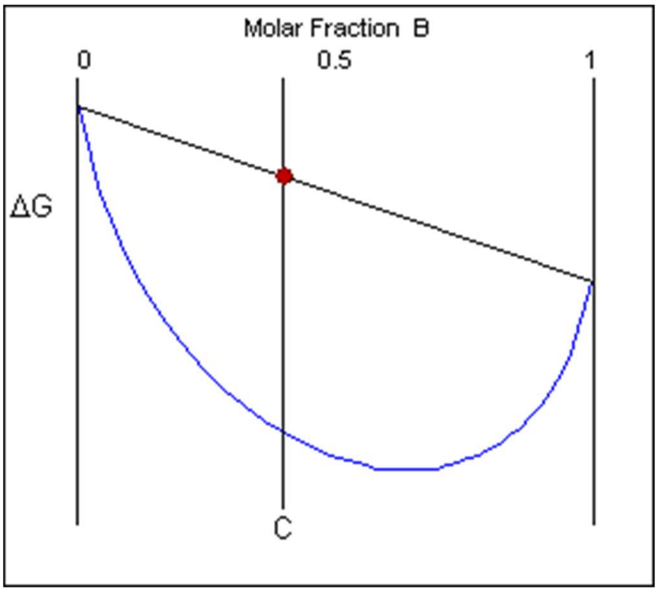

Figure 4 The molar free energy curve for the *α (solution)* phase,

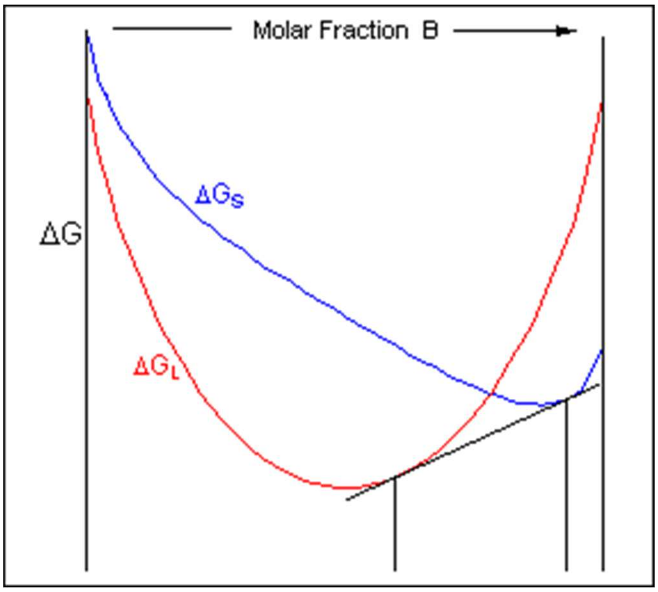

Figure 5 Molar free energy curves for solid and liquid phases and application of common tangent at an equilibrium.

When the temperature is altered the compositions of the solid and liquid in equilibrium change and build up the shape of the solidus and liquidus curves on a phase diagram. In figure 6, a binary system can be seen along with the free-energy curves for the liquid and solid phases at a range of temperatures shown on the phase diagram.

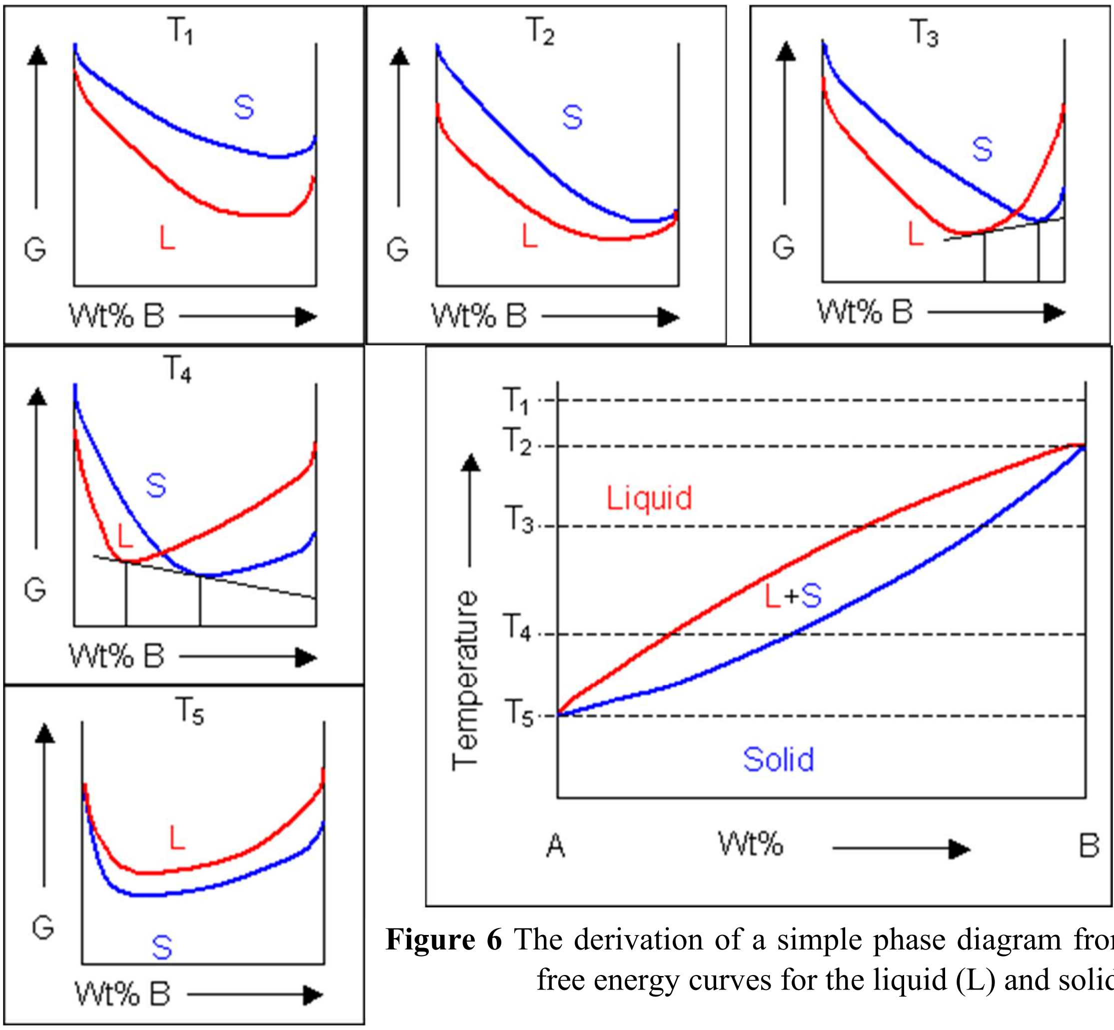

Figure 6 The derivation of a simple phase diagram from the free energy curves for the liquid (L) and solid (S).

2.5.2 Simple eutectic Systems

The free-energy curves and phase diagrams discussed in a simple phase diagrams were all for systems where the solid exists as a solution at all compositions and temperatures. In most real systems this is not the case. This is due to a positive ΔH_{mix} caused by unfavourable interactions between unlike neighbour atoms. As the temperature is reduced the ΔH_{mix} term becomes more significant and the curve turns upward at intermediate compositions, resulting in a curve with two minima and one maximum as described earlier. A common tangent can then be drawn between the two minima showing that the system can reduce its free energy through existing as a mixture of two distinct phases.

The free energy of a system of composition C_o can be minimised by existing as a mixture of two solid phases of composition C_1 and C_2:

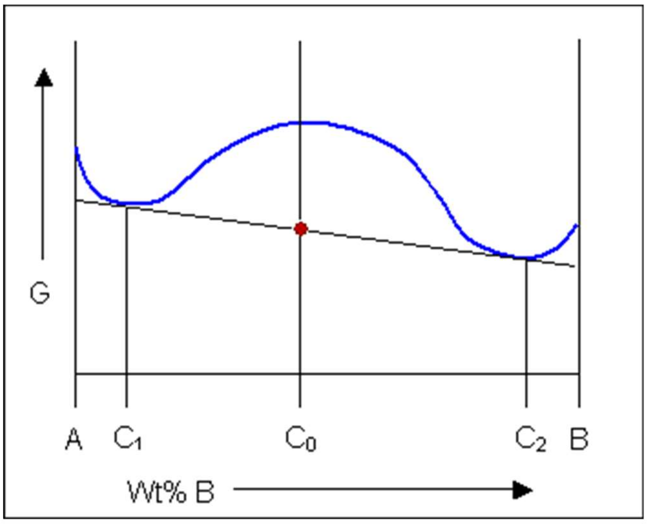

Figure 7 At equilibrium, alloy C_0 has a minimum free energy G_0 when it is a mixture of $C_1 + C_2$.

This effect can result in a system which, though single-phase upon solidification, will separate into two solid phases on cooling (e.g. Cr-W).

Another possible result is that the free-energy curve for the liquid will intersect the up turned section of the free-energy curve for the solid before the temperature is high enough to induce the formation of a solid solution. As the temperature is increased, the free-energy curve for the liquid moves downward relative to the solid curve and reaches a position where it is possible to link two parts of the solid free energy curve and one part of the liquid free energy curve with a common tangent. At this temperature three phases are in equilibrium. Here the system is at the eutectic temperature and three phases can be joined by a common tangent:

This is known as the eutectic temperature. At this temperature there will be a composition which solidifies at a single temperature through the co-operative growth of the two solid phases. This is the eutectic composition. It is this composition which will exhibit the lowest melting point for the system.

At temperatures above that of the eutectic there will be two common tangents producing two two-phase regions at the same temperature. The two different solid phases are commonly labeled as α and β. Eutectic systems therefore have a liquidus which contains a V to the eutectic point where it meets the eutectic invariant-reaction line.

Here is an example of a eutectic phase diagram. α and β are both solid phases. The two-phase solid region on the phase diagram will consist of a mixture of eutectic and either α or β phase depending on the whether the alloy composition is hypoeutectic or hypereutectic. The constitution of an alloy under equilibrium conditions can be found from its phase diagram.

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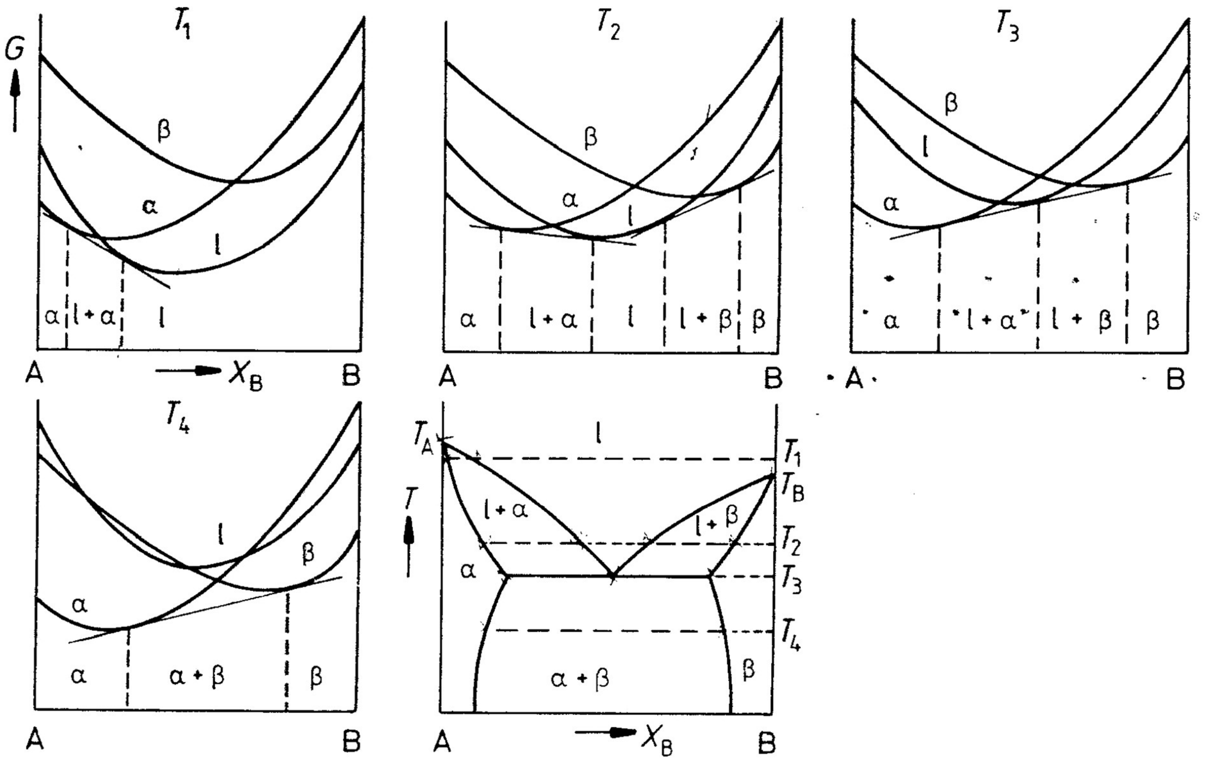

Figure 8 The derivation of a eutectic phase diagram where each solid phase has a different crystal structure.

2.6 INTERPRETATION OF COOLING CURVES

The melting temperature of any pure material (a one-component system) at constant pressure is a single unique temperature. The liquid and solid phases exist together in equilibrium only at this temperature. When cooled, the temperature of the molten material will steadily decrease until the melting point is reached.

At this point the material will start to crystallise, leading to the evolution of latent heat at the solid liquid interface, maintaining a constant temperature across the material. Once solidification is complete, steady cooling resumes. The arrest in cooling during solidification allows the melting point of the material to be identified on a time-temperature curve.

Most systems consisting of two or more components exhibit a temperature range over which the solid and liquid phases are in equilibrium. Instead of a single melting temperature, the system now has two different temperatures, the liquidus temperature and the solidus temperature which are needed to describe the change from liquid to solid.

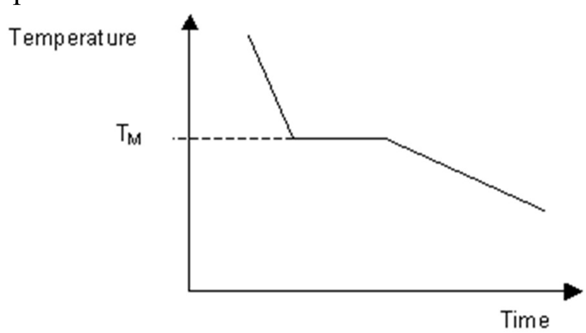

Figure 9 The temperature-time curve for pure substance.

The liquidus temperature is the temperature above which the system is entirely liquid, and the solidus is the temperature below which the system is completely solid. Between these two points the liquid and solid phases are in equilibrium. When the liquidus temperature is reached, solidification begins and there is a reduction in cooling rate caused by latent heat evolution and a consequent reduction in the gradient of the cooling curve.

Upon the completion of solidification the cooling rate alters again allowing the temperature of the solidus to be determined. As can be seen on the diagram below, these changes in gradient allow the liquidus temperature T_L, and the solidus temperature T_S to be identified.

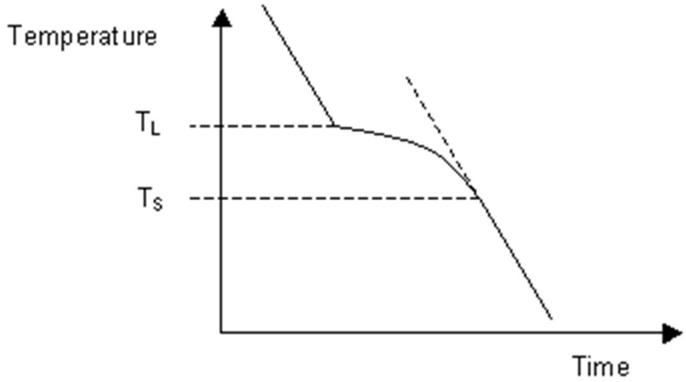

Figure 10 The temperature-time curve for two components system.

When cooling a material of eutectic composition, solidification of the whole sample takes place at a single temperature. This results in a cooling curve similar in shape to that of a single-component system with the system solidifying at its eutectic temperature.

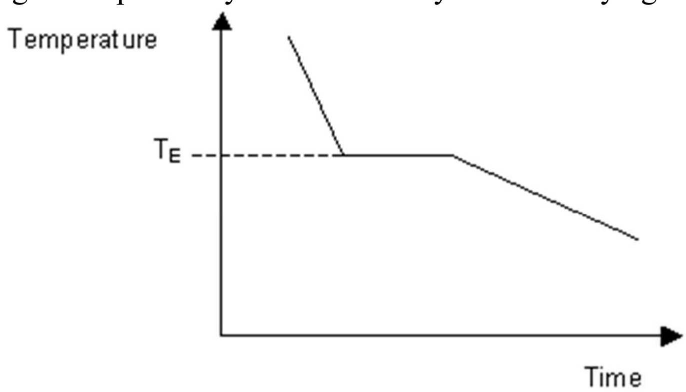

Figure 11 The temperature-time curve for a binary eutectic system at the eutectic composition.

When solidifying hypoeutectic or hypereutectic alloys, the first solid to form is a single phase which has a composition different to that of the liquid. This causes the liquid composition to approach that of the eutectic as cooling occurs. Once the liquid reaches the eutectic temperature it will have the eutectic composition and will freeze at that temperature to form a solid eutectic mixture of two phases.

Formation of the eutectic causes the system to cease cooling until solidification is complete. The resulting cooling curve shows the two stages of solidification with a section of reduced gradient where a single phase is solidifying and a plateau where eutectic is solidifying.

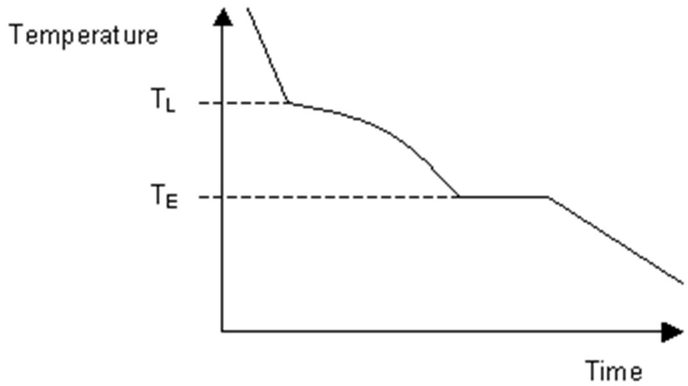

Figure 12 The temperature-time curve for a binary eutectic system under or above the eutectic composition.

By taking a series of cooling curves for the same system over a range of compositions the liquidus and solidus temperatures for each composition can be determined allowing the solidus and liquidus to be mapped to determine the phase diagram.

Below are cooling curves for the same system recorded for different compositions and then displaced along the time axis. The red regions indicate where the material is liquid, the blue regions indicate where the material is solid and the green regions indicate where the solid and liquid phases are in equilibrium.

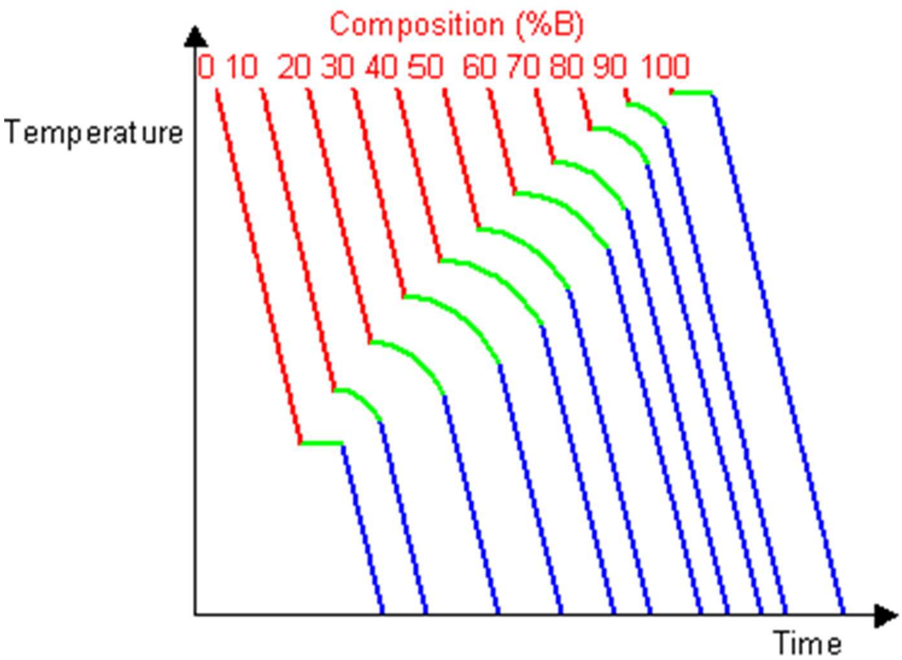

Figure 13 The temperature-time curves for a binary eutectic system at different compositions.

By removing the time axis from the curves and replacing it with composition, the cooling curves indicate the temperatures of the solidus and liquidus for a given composition. This allows the solidus and liquidus to be plotted to produce the phase diagram:

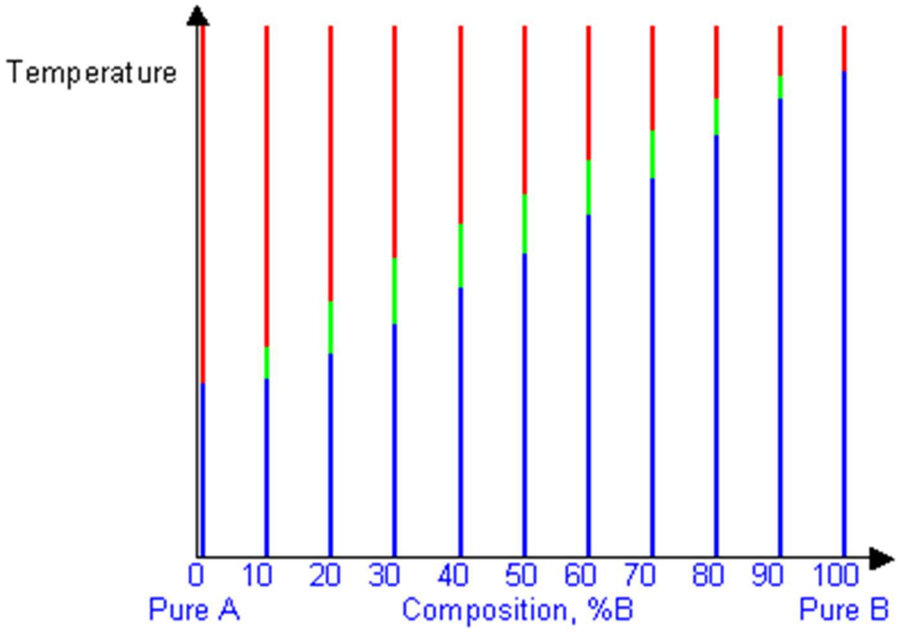

Figure 14 The derivation of a simple phase diagram from cooling curves.

3. EQUIPMENT AND MATERIALS

Equipment: Vacuum melting Furnace, Data Logger, Computer (Laptop or PC)
Materials: Metals (Pb and Sn), Graphite crucible, thermocouples (K type)

4. EXPERIMENTAL PROCEDURE

The simplest way to construct a phase diagram is by plotting the temperature of a liquid against time as it cools and turns into a solid. As discussed in Interpretation of cooling curves, the solidus and liquidus can be seen on the graphs as the points where the cooling is retarded by the emission of latent heat.

An experiment can be performed to get a rough idea of a phase diagram by recording cooling curves for alloys of two metals, in various compositions. The alloy chosen for this example is tin-lead (Sn-Pb), both of which metals have low melting points, and so can be heated and cooled more quickly and easily in the lab. So that the experiment could be performed in a reasonable time, 3 compositions were used, from pure tin to lead in steps of 10%. All the compositions were measured in weight percent.

A sufficient amount of metallic materials were melted in a vacuum furnace to produce a molten alloy which has desired composition in a graphite crucible, approximately 100 mm in length and 30 mm in diameter by using Pb and Sn. The vacuum melting furnace picture is shown in Figure 22 and can be operated up 11000°C. The purity of Sn and Pb were 99.99%. After stirring, the graphite crucible including the molten metallic alloy is taken out and the graphite lid with thermocouple is placed at the top of the crucible. The end of thermocouple is connected to data logger to record the temperature-time curve of molten alloy. The cooling curve record system is schematically shown in Figure 23. When the temperature of metallic alloy reaches 20 Celsius degree below the melting temperature of alloy the record is stopped.

Figure 22. Vacuum melting furnace.

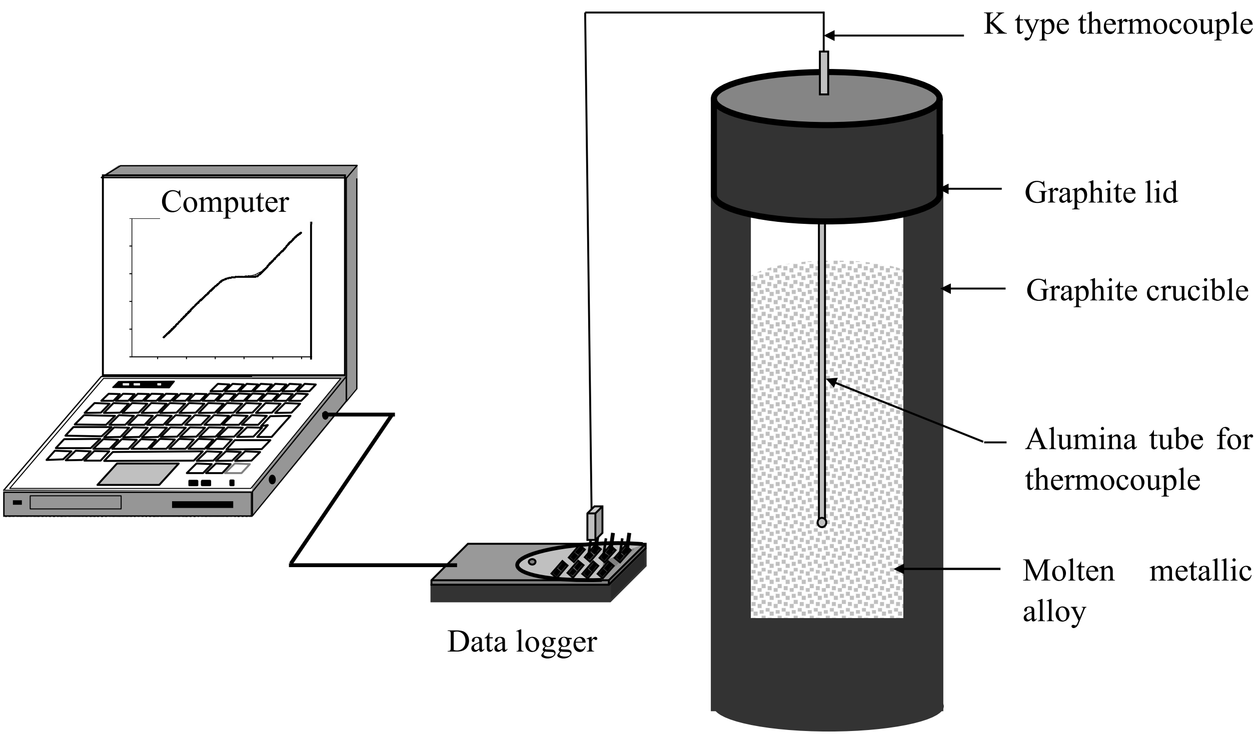

Figure 23. Schematic illustration a typical experimental set up to obtain the cooling curves of metallic alloys

The Pb-Sn binary system phase diagram is shown in Figure 24.

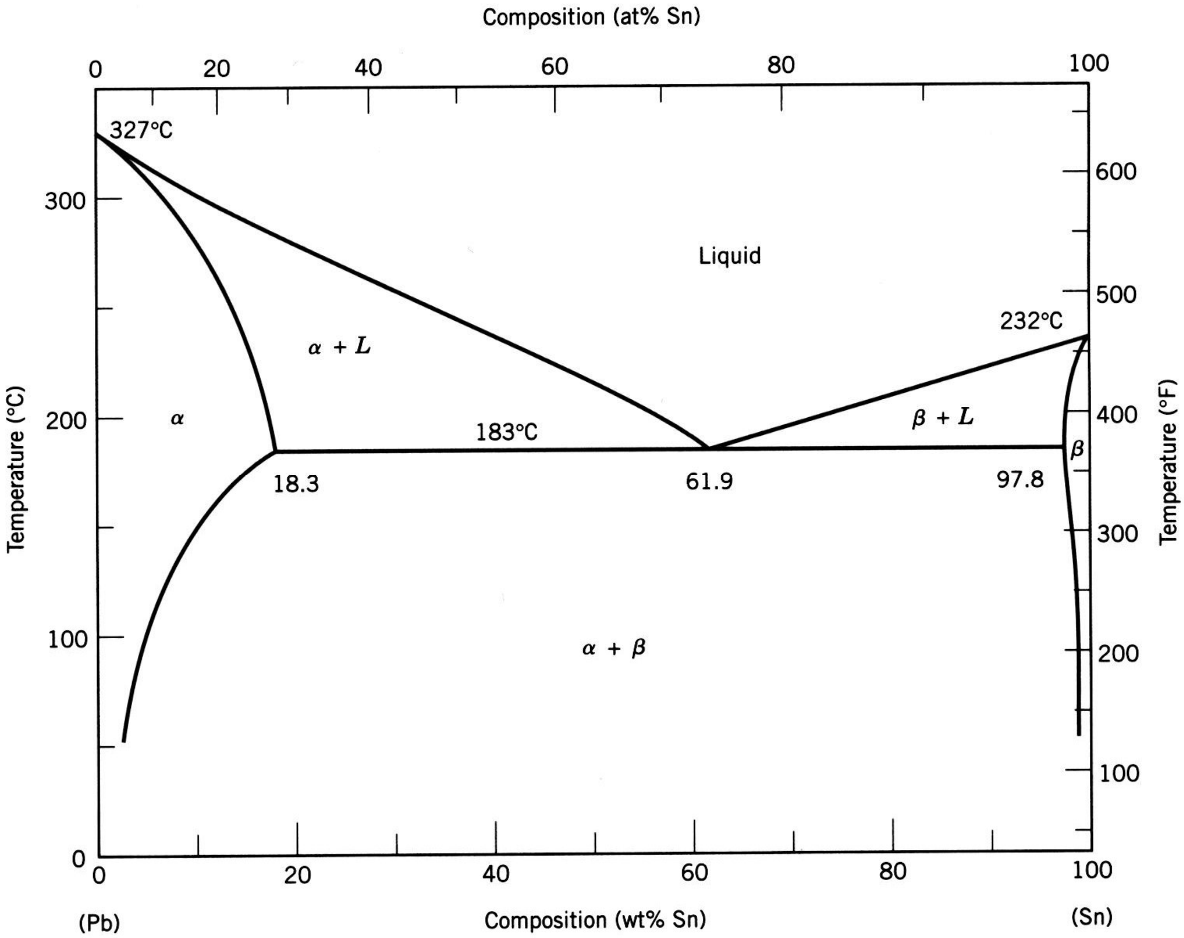

Figure 2 4. The phase diagram of Pb-Sn binary system.

5. ASSIGNMETNS AND REQUESTS

1. Give same details about the experimental method and procedure for binary phase diagram
2. Plot the phase diagram of Sn reach side of Sn-Pb binary alloy by using the measured solidus and liquidus temperatures for three different composition of Sn-Pb binary system.

6. REFERENCES

1. Porter, D. A. and Easterling K, *Phase Transformations in Metals and Alloys*, 2nd edition, Routledge, 1992.
2. Smallman, R. E, *Modern Physical Metallurgy*, Butterworth, 1985.
3. John, V, *Understanding Phase Diagrams*, Macmillan,1974.

4. CASTING

1. Aim

The purpose of this experiment is to introduce the casting method in general, to give information about the casting processes and to give hand skills about the production of sand molds.

2. Theoretical Information

A casting is a metal object produced by solidifying molten metal in a mold. The shape of the object is determined by the shape of the mold cavity. The casting process, also known as founding, involves melting metal and pouring it into the mold cavity, which is close to the final dimensions of the finished form. Many types of complex objects ranging in size from a few grams to thousands of kilograms are produced in a metal casting facility. Castings are produced by various casting processes such as sand, permanent mold, investment, and lost foam. While all metals can be cast, the most predominant are iron, steel, aluminum, copper, magnesium, and zinc-based alloys. Metal castings are used in more than 90% of all manufactured goods and find a wide range of applications in various sectors such as transportation (automotive, rail-way, naval, aerospace), mining, forestry, power generation, petrochemical, construction machinery, sporting goods, household appliances, and farm equipment.

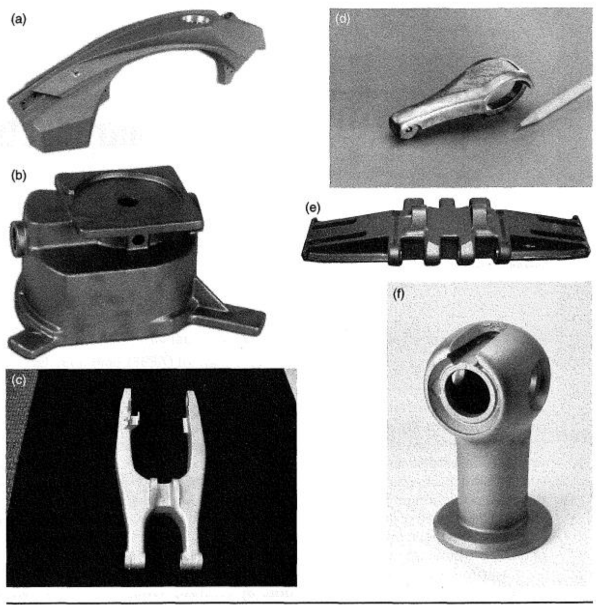

Figure 1 *Typical castings in major alloys,* ***(a)*** *This motorcycle frame component was produced via the nobake sand casting process in 356 aluminum with T6 treatment temper,* ***(b)*** *The bronze alloy used for this dental suction pump was selected for its high strength, mechanical properties, and wear resistance,* ***(c)*** *Produced for a racing motorcycle, this one-piece magnesium casting replaced a three-piece aluminum part. The component is 33% lighter than the original, which impacts the overall performance of the bike,* ***(d)*** *This miniature zinc casket arm weighs less than 6 oz.* ***(e)*** *This NASA component for the space shuttle crawler transporter, produced with modified 4320 steel alloy via V-process casting, met reduced surface hardness requirements while maintaining high material strength,* ***(f)*** *This ductile iron green sand casting is the main structural element of the Spartan hydrant, enclosing and protecting its working parts.*

2.

CASTING

Certain advantages are inherent in the metal casting processes. These may form the basis for choosing casting as a process to be preferred over other shaping processes. Some of the reasons for the success of the casting process are as follows:

- The most intricate of shapes, both external and internal, may be cast. As a result, many other manufacturing operations such as machining, forging, and welding may be minimized or eliminated.
- Because of their metallurgical nature, some metals can only be cast to shape since they cannot be hot-worked into bars, rods, plates, or other shapes from ingot form as a preliminary to other processing. A good example of casting is the family of cast irons which are low cost, extremely useful, and exceed the total of other metals in tonnage cast.
- Casting is a simplified manufacturing process. An object cast as a single piece often would otherwise require multiple manufacturing steps (stamping and welding, for example) to be produced any other way.
- Casting can be a low-cost, high-volume production process, where large numbers of a given component may be produced rapidly. Typical examples are plumbing parts and automotive components such as engine blocks, manifolds, brake calipers, steering knuckles, and control arms.
- Extremely large, heavy metal objects such as pump housings, valves, and hydroelectric plant parts which could weigh up to 200 tons may be cast. These components would be difficult or economically impossible to produce otherwise.
- Some engineering properties such as machinability, bearing, and strength are obtained more favorably in cast metals. In addition, more uniform properties from a directional standpoint can be expected, which is not generally true for wrought products.
- Casting technology has progressed significantly, allowing products to be cast with very thin cross sections, often referred to as "thin-wall-casting"; such capabilities allow designers to reduce the casting weight that is often assumed necessary for production.
- One has to consider the economic advantages of the casting process. In the aerospace industry, some components are still being machined out of forged or rolled pieces despite the fact such pieces can be cast more eco-nomically to meet the design criteria, especially with respect to strength and toughness.

Table 1 World Production of Castings during 2009 to 2011 (in metric tons)

Metal	2009	2010	2011
Gray iron	37,749	43,258	45,870
Ductile iron	29,404	23,451	24,782
Malleable iron	1,013	–	–
Steel	9,070	10,215	10,342
Copper alloys	1,488	1,652	1,799
Aluminum alloys	9,477	10,879	11,319
Magnesium alloys	149	196	181
Zinc alloys	470	528	505
Total	80,895	91,673	98,593

Source: From Spada [3].

Note: Global forecast is for 102 million tons by 2015.

2.2 Casting Terms

***1. Flask**:* A metal or wood frame, without fixed top or bottom, in which the mold is formed. Depending upon the position of the flask in the molding structure, it is referred to by various names such as drag-lower molding flask, cope-upper molding flask, cheek-intermediate molding flask used in three piece molding.

2. Pattern: It is the replica of the final object to be made. The mold cavity is made with the help of pattern.

3. Parting line: This is the dividing line between the two molding flasks that makes up the mold.

4. Molding sand: Sand, which binds strongly without losing its permeability to air or gases. It is a mixture of silica sand, clay, and moisture inappropriate proportions.

5. Facing sand: The small amount of carbonaceous material sprinkled on the inner surface of the mold cavity to give a better surface finish to the castings.

6. Core: A separate part of the mold, made of sand and generally baked, which is used to create openings and various shaped cavities in the castings.

7. Pouring basin: A small funnel shaped cavity at the top of the mold into which the molten metal is poured.

8. Sprue: The passage through which the molten metal, from the pouring basin, reaches the mold cavity. In many cases it controls the flow of metal into the mold.

9. Runner: The channel through which the molten metal is carried from the sprue to the gate.

10. Gate: A channel through which the molten metal enters the mold cavity.

11. Chaplets: Chaplets are used to support the cores inside the mold cavity to take care of its own weight and overcome the metallostatic force.

12. Riser: A column of molten metal placed in the mold to feed the castings as it shrinks and solidifies. Also known as "feed head".

13. Vent: Small opening in the mold to facilitate escape of air and gases.

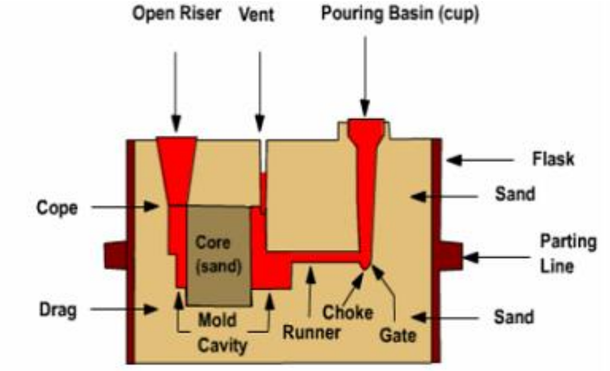

Figure 2 Mold section

2.3 Casting Process

Practically all the detailed operations that enter into the making of sand castings may be categorized as belonging to one of five fundamental steps of the process:

1. Pattern making (including core boxes)
2. Core making
3. Molding
4. Melting and pouring
5. Cleaning

2.3.1 Pattern making

Patterns are required to make molds. The mold is made by packing some readily formed plastic material, such as molding sand, around the pattern. When the pattern is withdrawn, its imprint provides the mold cavity, which is ultimately filled with metal to become the casting. Thus molding requires, first, that patterns to be made. A pattern, as shown in Figure 2, may be simply visualized as an approximate replica of the exterior of a casting. If the casting is to be hollow, as in the case of a pipe fitting, additional patterns, referred to as core boxes, are used to form the sand that is used to create these cavities.

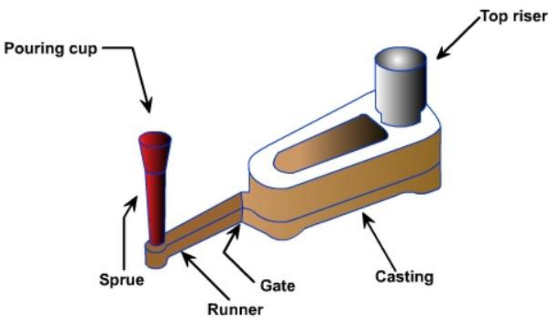

Figure 3 Pattern

Patterns may be constructed from the following materials. Each material has its own advantages, limitations, and field of application. Some materials used for making patterns are: wood, metals and alloys, plastic, plaster of Paris, plastic and rubbers, wax, and resins. To be suitable for use, the pattern material should be:

1. Easily worked, shaped and joined
2. Light in weight
3. Strong, hard and durable
4. Resistant to wear and abrasion
5. Resistant to corrosion, and to chemical reactions
6. Dimensionally stable and unaffected by variations in temperature and humidity
7. Available at low cost

The usual pattern materials are wood, metal, and plastics. The most commonly used pattern material is wood, since it is readily available and of low weight. Also, it can be easily shaped and is relatively cheap.

2.3.2 Core Making

Most simply defined, cores are sand shapes which form the contour of a casting that is not molded with a pattern. Forming internal cavities thus depends mainly on cores which can be inserted into a mold of the casting exterior. Through their use in forming complex internal cavities, cores provide the casting process its ability to make the most intricate of shapes, eliminate much machining, and in fact produce shapes which would be impossible to machine.

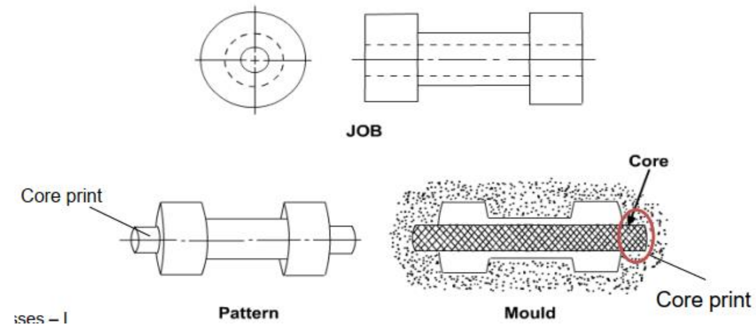

Figure 4 Core

Cores may be made of metal, plaster, and investment and ceramic materials, as well as core sand. To achieve the utmost of intricacy in castings, cores must be collapsible after the metal is poured. Metal ores, used in permanent-mold, or die casting, do not have collapsibility and therefore have shape limitations. However, sand cores and some other materials do not have this handicap and can therefore produce almost any desired degree of casting intricacy. Sand cores, along with sand molding, are the most frequently used.

2.3.3 Molding

Molding consists of all operations necessary to prepare a mold for receiving molten metal.

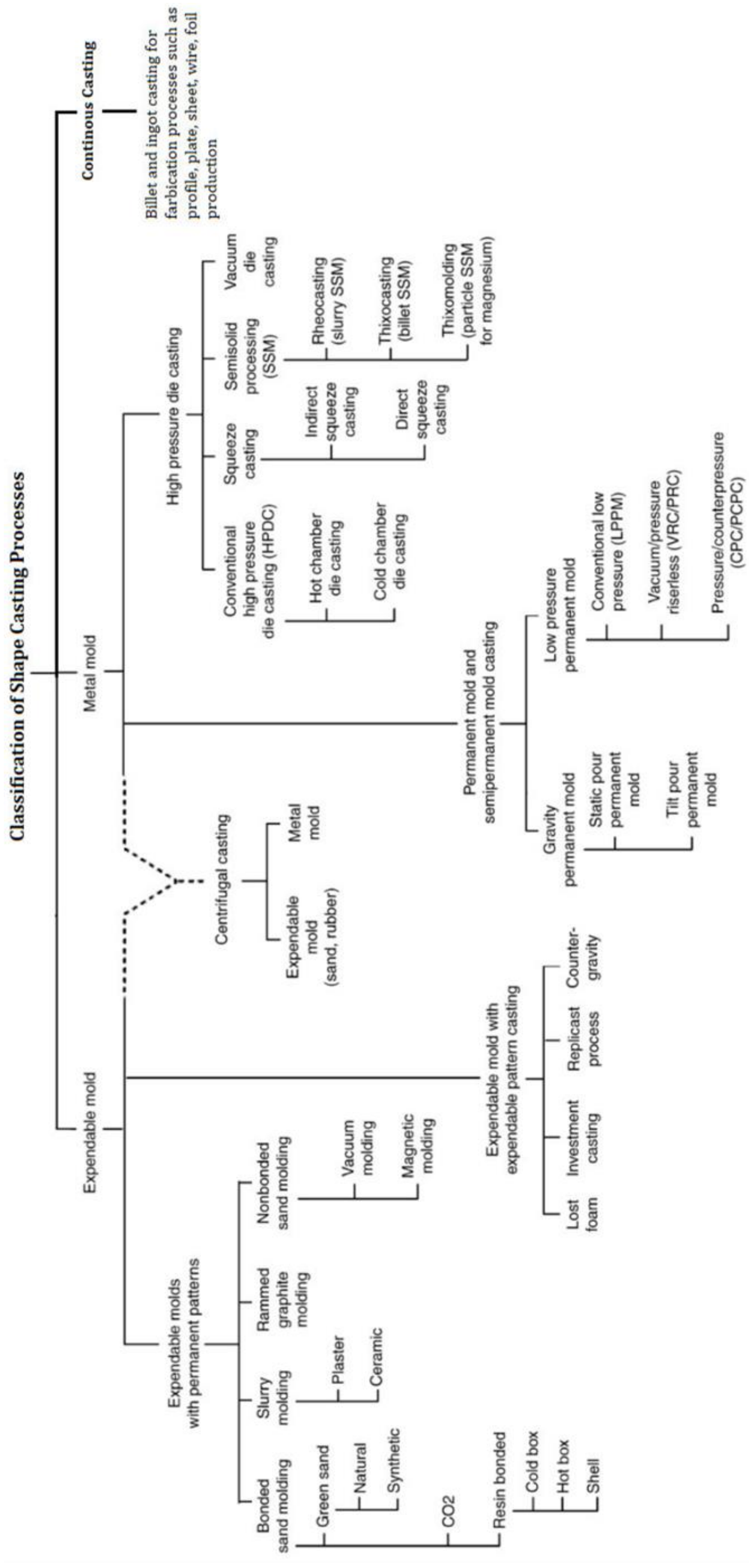

***Figure* 5** Classification of casting processes

Sand Casting

Sand casting, the most widely used casting process, utilizes expendable sand molds to form complex metal parts that can be made of nearly any alloy. Because the sand mold must be destroyed in order to remove the part, called the casting, sand casting typically has a low production rate. The sand casting process involves the use of a furnace, metal, pattern, and sand mold. The metal is melted in the furnace and then ladled and poured into the cavity of the sand mold, which is formed by the pattern. The sand mold separates along a parting line and the solidified casting can be removed. Sand casting is used to produce a wide variety of metal components with complex geometries. These parts can vary greatly in size and weight, ranging from a couple ounces to several tons. Some smaller sand cast parts include components as gears, pulleys, crankshafts, connecting rods, and propellers. Larger applications include housings for large equipment and heavy machine bases. Sand casting is also common in producing automobile components, such as engine blocks, engine manifolds, cylinder heads, and transmission cases.

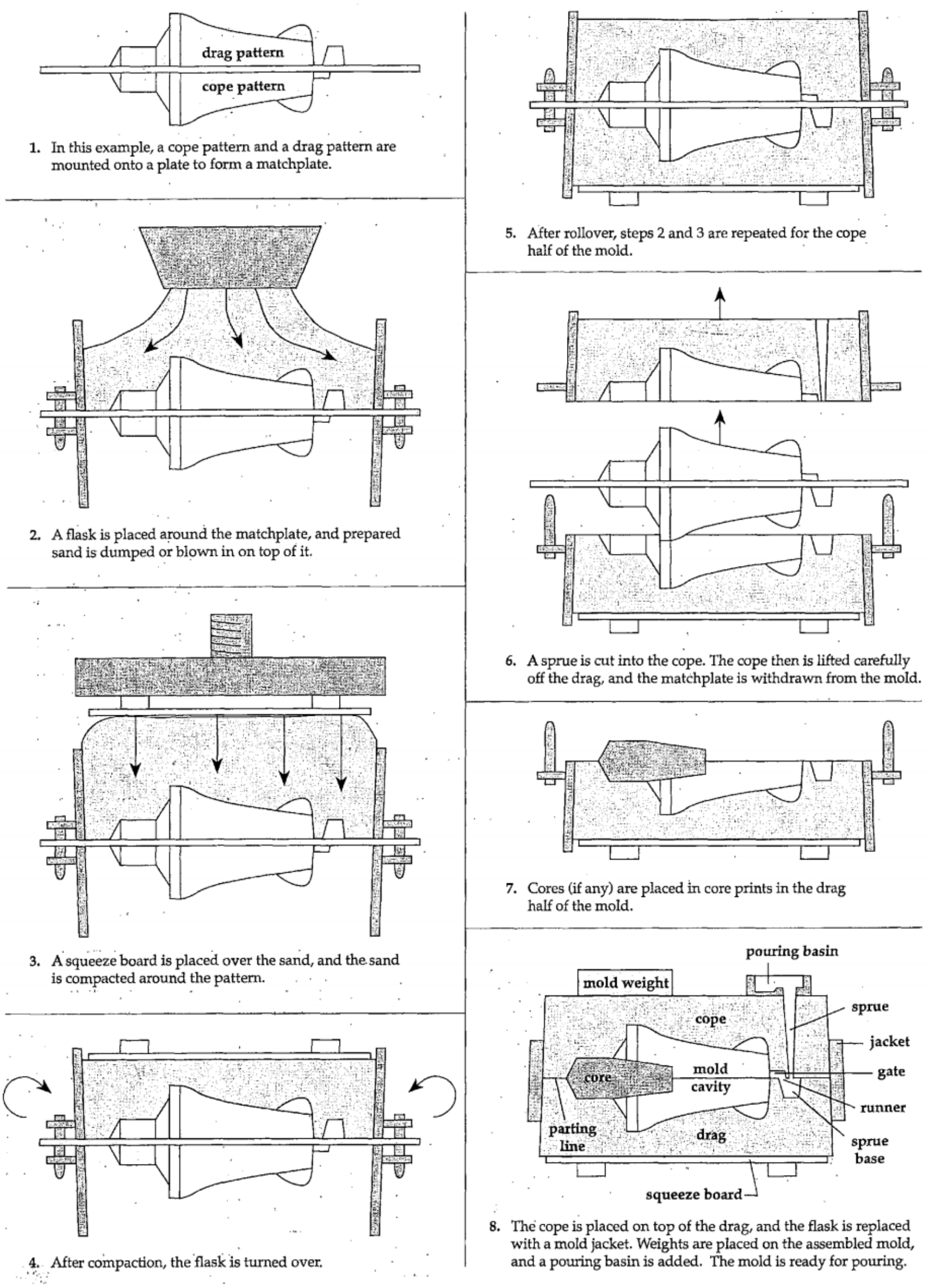

Figure 6 Steps of making sand mold

a) Molding Material and Properties

A large variety of molding materials is used in foundries for manufacturing molds and cores. They include molding sand, system sand or backing sand, facing sand, parting sand, and core sand. The choice of molding materials is based on their processing properties. The properties that are generally required in molding materials are:

Refractoriness: It is the ability of the molding material to resist the temperature of the liquid metal to be poured so that it does not get fused with the metal. The refractoriness of the silica sand is highest.

Permeability: During pouring and subsequent solidification of a casting, a large amount of gases and steam is generated. These gases are those that have been absorbed by the metal during melting, air absorbed from the atmosphere and the steam generated by the molding and core sand. If these gases are not allowed to escape from the mold, they would be trapped inside the casting and cause casting defects. To overcome this problem the molding material must be porous. Proper venting of the mold also helps in escaping the gases that are generated inside the mold cavity.

Green Strength: The molding sand that contains moisture is termed as green sand. The green sand particles must have the ability to cling to each other to impart sufficient strength to the mold. The green sand must have enough strength so that the constructed mold retains its shape.

Dry Strength: When the molten metal is poured in the mold, the sand around the mold cavity is quickly converted into dry sand as the moisture in the sand evaporates due to the heat of the molten metal. At this stage the molding sand must possess the sufficient strength to retain the exact shape of the mold cavity and at the same time it must be able to withstand the metallostatic pressure of the liquid material.

Hot Strength: As soon as the moisture is eliminated, the sand would reach at a high temperature when the metal in the mold is still in liquid state. The strength of the sand that is required to hold the shape of the cavity is called hot strength.

Collapsibility: The molding sand should also have collapsibility so that during the contraction of the solidified casting it does not provide any resistance, which may result in cracks in the castings. Besides these specific properties the molding material should be cheap, reusable and should have good thermal conductivity.

b) Molding Sand Composition

The main ingredients of any molding sand are; base sand, binder, and moisture.

Base Sand: Silica sand is most commonly used base sand. Other base sands that are also used for making mold are zircon sand, Chromite sand, and olivine sand. Silica sand is cheapest among all types of base sand and it is easily available.

Binder: Binders are of many types such as; clay binders, organic binders and inorganic binders. Clay binders are most commonly used binding agents mixed with the molding sands to provide the strength. The most popular clay types are kaolinite or fire clay ($Al_2O_3.2SiO_2.2H_2O$) and bentonite ($Al_2O_3.4SiO_2.nH_2O$). Bentonite can absorb more water which increases its bonding power.

Moisture: Clay acquires its bonding action only in the presence of the required amount of moisture. When water is added to clay, it penetrates the mixture and forms a microfilm, which coats the surface of each flake of the clay. The amount of water used should be properly controlled. This is because a part of the water, which coats the surface of the clay flakes, helps in bonding, while the remainder helps in improving the plasticity. A typical composition of molding sand is given in Table 2.

Table 2 Composition of molding sand

Molding Sand Constituent	Weight Percent
Silica Sand	92
Clay	8
Water	4

c) Advantages and Disadvantages of Sand Molding

Advantages of sand molding are:

1) Suitable for casting iron and non-ferrous metal alloys.
2) Sand mold is a suitable method for both small and large parts.
3) Mold material is cheap and abundant.
4) Suitable for a small number of parts.
5) Molding cost is the lowest casting method.

Disadvantages of sand molding are:

1) Not suitable for mass production.
2) Surface and size accuracy is not good.
3) Very fine details are difficult to obtain.
4) The parts obtained from the casting are subjected to other processes.
5) Molding causes large time loss.
6) Material consumption is phase.

2.3.4 Melting

Melting is an equally important parameter for obtaining a quality castings. A number of furnaces can be used for melting the metal, to be used, to make a metal casting. The choice of furnace depends on the type of metal to be melted.

2.3.5 Cleaning

Cleaning refers to all operations necessary to the removal of sand, scab and excess metal from the casting. The casting is separated from the molding sand and transported to the cleaning department. Burned sand and scale are removed to improve the surface appearance of the casting. Excess metal, in the form of fins, wires, parting-line fins, and gates, is cut off. Defective castings may be salvaged by welding or other repair. Inspection of the casting for defects and general qualify follows. The casting is then ready for shipment or further processing for example, heat-treatment, surface treatment, or machining.

3. Experimental Procedure

3.1 Mold Making

• A specified amount of sand, bentonite and water are loaded into the large sand mixer.
• It is mixed until it becomes suitable for molding.

• Top and bottom are placed on top of the molding plate.
• The pattern is placed between two flasks.
• Graphite is sprinkled on the pattern.
• Flask is filled with sand.
• Gradually compact the sand with hand tools and air hammer.
• Cope and drag are separated and pattern extracted.
• If necessary, the mold is repaired.
• The cope and drag are reassembled and ready for casting.

3.2 Casting

• The prepared mold is brought to the front of the melting furnace.
• Sand is poured around the mold and weights are placed on it.
• The crucible is removed from the furnace and slag skimmed.
• The liquid metal is poured into the mold.
• The mold is broken to remove the casting.

4. Requirements

1. List the properties and differences of casting and core sands

2. Briefly explain semi-solid casting methods.

3. Write down the causes of casting defects and write down the precautions to be taken.

4. Explain the cast iron types and their mechanical properties

5. Write the alloying elements and functions used in cast iron.

6. Write down the classification of aluminum casting alloys.

7. Describe the grain refinement, eutectic modification, degassing and fluxing processes in aluminum casting.

8. Write down the alloying elements and their functions used in aluminum casting alloys.

5. Referances

[1] Sahoo M, Sahu S, "*Principles of Metal Casting",* Third Edition, McGraw-Hill Education, Printed in the United States of America, 2014.

[2] Jorstad JL, Rasmussen WM, "Aluminum Casting Technology", Second Edition, AFS.

[3] Cigdem M, Casting Technology lecture notes.

MEASUREMENT AND CALIBRATION

1. Objective Of The Experiment

Dimension checks of parts of the production with the use of calipers and micrometers.

2. Fundamentals of Metrology and Measurement Techniques

The measurement technique is used to solve technical problems. The theoretical hypotheses are supported by the necessary tests and observations.

Metrology is the science of measurement. Metrology covers all practical and theoretical topics based on measurement, regardless of level of accuracy and application.

In modern manufacturing systems such as lean manufacturing, intelligent production, interchangeable manufacturing technology, measuring technique for quality products, production and quality manufacturing processes is a foundation and inevitable. The system should be evaluated as a whole, the products manufactured in different places must comply with the specified specifications and production must be realized in a unit of measure.

Recognition of the measurement of a measurement instrument used in the industry worldwide and acceptance that it is the same as the other measurements are possible with this measurement reaching the highest precision basic measurement standard with a measurement reference chain..

3. Quality control

Conducting quality control; to develop, design, produce and maintain a quality product that is most economical, most useful and always satisfies the consumer (K.ISHIKAWA). In order to achieve this goal, everyone in the company, including all departments within the company and all employees, should participate in quality control and help improve it.

The first step in quality control is to know consumers' wishes. Another step in quality control is to know what consumers will buy. Quality cannot be defined without knowing the cost.

It is possible to carry out the production process under the desired quality and quality uniformity in the most economical and reliable way but by applying statistical quality control methods. Quality control ensures that the products obtained at the end of the production process comply with the required standards, and products that do not meet the standards are either corrected by some operations, sold or destroyed at low prices.
Accordingly, the purpose of quality control; to prevent non-standard production or to reduce to an unimportant level. Statistical quality control; In the event that production is out of control due to a failure or a special reason, playing a very important role in ensuring the production and execution of the production process under normal circumstances is the

application of the methods that ensure that the necessary measures are taken in a timely manner. To sum up, these methods were the top producer of the manufacturing process to give the desired direction.

4. Statistical Quality Control

Increasing consumer needs and, in parallel with the expanding production volume, the implementation of an inspection-based inspection system is sometimes impossible, and at times it becomes cost-effective.

First development W.A. Shewhart's "Control schemes" were implemented with Dodge and Romig's "Sampling with inspection" systems. This is simple, but highly effective tools and systems were based on statistical sampling. With the widespread use of these tools, "Statistical Process Supervision-Control-SPC" under the name of methods to minimize the production of faulty production with sampling methods have been successfully applied to the present day.

There are three major areas where statistical techniques are used extensively. These,
1. Control of raw or semi-finished goods purchased externally (INPUT CONTROL)
2. Control of material or product sent to external organizations or other parts of the organization (OUTPUT CONTROL)
3. Control during production (PROCESS-Process-control)

In the first two of these techniques are called ACCEPTING SAMPLES, the last one is CONTROL GRAPHICS. In many cases, the quality of the goods accepted by the Acceptance sampling method is better than that accepted by the 100% inspection.
Because of the 100% examination of the effects of tedious and intensity-causing quality is reduced. However, 100% inspection of some critical parts which are not suitable for sampling is inevitable. Costs related to quality are of great importance for every producer organization.

The objective of statistical quality control is to keep the process in a controlled and acceptable condition. Thus, the products will be guaranteed to comply with the requested criteria.

Quality control cards form the basis of statistical process control. Quality control cards are useful visual aids for controlling and controlling the process.

5. Quality Control Cards

Diagrams called the Shewhart forms the basis for the control cards. In such diagrams, data taken from the production process at regular intervals are processed. These ranges can be either time (hours) or as a measure of quantity (number of pieces). Quality control cards indicate whether a process is running under statistical control, whether the process has been mastered. Quality control cards allow random and systematic changes to be distinguished from each other. In this way, systematic changes are determined and compensation is provided with the adjustments made in the process.

6. Materials And Equipment Used In The Experiment

- Mechanical Caliper
- Mechanical Micrometer
- Manufacturing Parts

7. Experimental Procedure

Example:
The samples were taken from an eccentric press machine. Technical figures of the inner diameter of the stamps are 13 ± 0.3 mm, the outer diameter is 23,80 ± 0.3 mm and the thickness value is 2.5 ± 0.3 mm. The inner diameter, outer diameter and thickness values were measured and written to the ICH table. The sample size is n = 5 and a sample group is taken from each tray and recorded by the operator to the table. By calculating the sum of each group of five, Xort. the average and the largest size to the smallest size interval, R is processed to the table .
The selection of the sample size to be taken at this time depends on the nature of the process. The general principle is that the probability of influencing the process during the sampling is as low as possible and that the differences between the products are affected only by general reasons. In this respect, it is generally preferred to take the 5 pieces produced in the form as a sample group..
-Arithmetic mean (x,) and range (R) - Quality control card without standard values:
-Determination of sample number
-Measurement of samples
-Calculation of arithmetic mean and range

Table 1. Calculation Of Measurement Values

Grup / Numune No.	A	B	C	D	E
1.	2,32	2,53	2,57	2,53	2,56
2.	2,31	2,62	2,53	2,55	2,34
3.	2,60	2,55	2,56	2,52	2,57
4.	2,52	2,36	2,58	2,26	2,27
5.	2,46	2,54	2,55	2,44	2,49
ΣX	12,21	12,60	12,79	12,31	12,23
$\overline{x_i}$	2,44	2,52	2,56	2,46	2,45
R_i	0,29	0,26	0,05	0,29	0,30

4.

$$\overline{x_i} = \frac{\sum X'}{n} = \overline{x_A} = \frac{12{,}21}{5} = 2{,}44; \quad \overline{x_B} = \frac{12{,}60}{5} = 2{,}52; \quad \overline{x_C} = \frac{12{,}79}{5} = 2{,}56 \ldots.$$

$$\overline{\overline{X}} = \frac{\overline{x_A} + \overline{x_B} + \overline{x_C} + \overline{x_D} + \overline{x_E}}{n} = 2{,}49$$

5.

$$R_i = R_{max} - R'_{min}; = \quad R_A = 2{,}60 - 2{,}31 = 0{,}29; \quad R_B = 2{,}62 - 2{,}36 = 0{,}26..$$

$$\overline{R} = \frac{R_A + R_B + R_C + R_D + R_E}{n} = 0{,}238$$

6. HARDENABILITY AND THE JOMINY TEST

Objective:

1. Distinguish between hardness and hardenability.
2. Understand the concept of mass effect and ruling section.
3. Perform Jominy test as a method to indicate hardenability.

Theoretical Knowledge:

Hardenability is the ability of an alloy to be hardened by the formation of martensite as a result of a given heat treatment. It is a qualitative measure of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content.With the Jominy end-quench test, except for alloy composition, a cylindrical specimen is austenitized and upon removal from the furnace, the lower end is quenched by a jet of water. The cooling rate is a maximum at the quenched end and diminishes with position from this point along the length of the specimen. With diminishing cooling rate more time is allowed for carbon diffusion and the formation of a greater portion of the softer pearlite or bainite. A steel alloy that is highly hardenable will retain large hardness values for relatively long distances. The presence of nickel, chromium, and molybdenum in the alloy steels delay the austenite-to-pearlite and/or bainite reactions, thus permitting more martensite to form for a particular cooling rate.

Factors Affecting Hardenability:

- Carbon Content
- Alloying elements
- Grain size
- Cooling rates

TTT diagrams for (a) hypoeutectoid, (b) eutectoid and (c) hypereutectoid steels are given in Fig. 1.

As the carbon percentage increases A_3 decreases, similar is the case for A_{r3}, i.e. austenite stabilises. So the incubation period for the austenite to pearlite increases i.e. the C curve moves to right. However after 0,8 wt%C any increase in C, A_{cm} line goes up, i.e. austenite become less stable with respect to cementite precipitation. So transformation to pearlite becomes faster. Therefore C curve moves towards left after 0,8%C.

Almost all alloying elements (except, Al, Co) increases the stability of supercooled austenite and retard both proeutectoid and the pearlitic reaction and then shift TTT curves of start to finish to right or higher timing. This is due to i) low rate of diffusion of alloying elements in austenite as they are substitutional elements, ii) reduced rate of diffusion of carbon as carbide forming elements strongly hold them.

However Al, and Co increase rate of nucleation and growth of both ferrite or pearlite and therefore shift TTT diagram to left. In addition under the complex diffusional effect of various alloying element the simple C shape behaviour of TTT diagram get modified and various regions of transformation get clearly separated. There are separate pearlitic C curves, ferritic and bainitic C curves and shape of each of them are distinct and different.

Fine grain size shifts S curve towards left side because it helps for nucleation of ferrite, cementite and bainite.

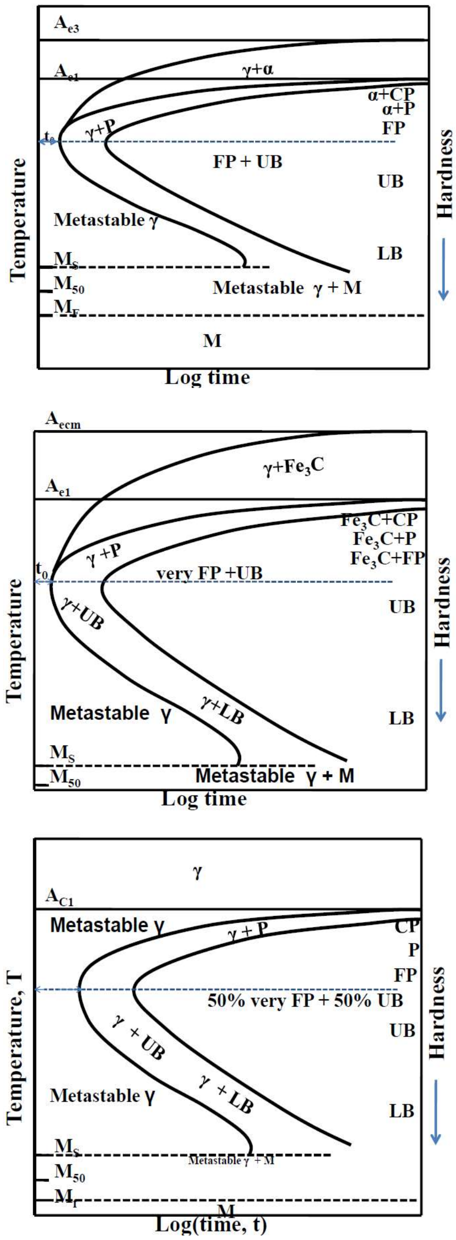

Figure 1. TTT diagrams for (a) hypoeutectoid, (b) eutectoid and (c) hypereutectoid steels

ASTM A 255 measures hardenability of steels. Hardenability is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature. Hardenability of a steel should not be confused with the hardness of a steel. The Hardness of a steel refers to its ability to resist deformation when a load is applied, whereas hardenability refers to its ability to be hardened to a particular depth under a particular set of conditions. Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes.

Experimental Procedure:

First, a sample specimen cylinder either 100mm in length and 25mm in diameter, or alternatively, 101.6 mm by 25.4 mm is obtained. Second, the steel sample is austenitised. This is usually at a temperature of 800 to 900°C. Next, the specimen is rapidly transferred to the test machine (Fig. 2), where it is held vertically and sprayed with a controlled flow of water onto one end of the sample. This cools the specimen from one end, simulating the effect of quenching a larger steel component in water. Because the cooling rate decreases as one moves further from the quenched end, you can measure the effects of a wide range of cooling rates from vary rapid at the quenched end to air cooled at the far end.

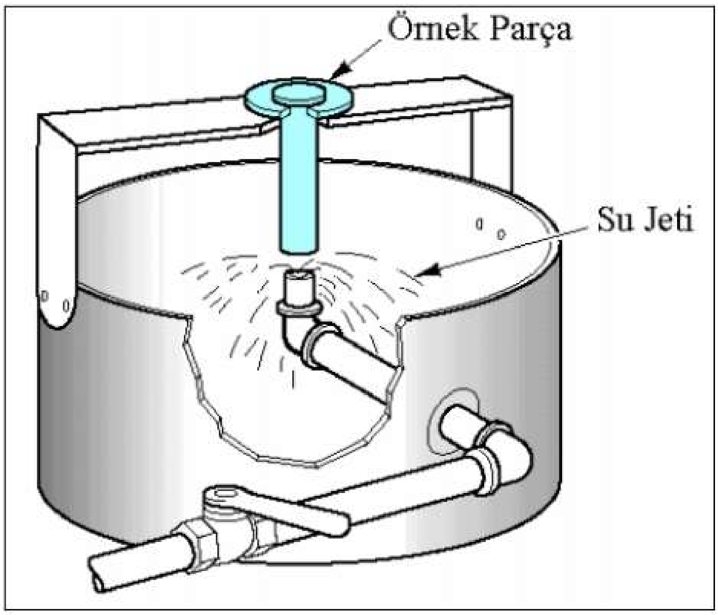

Figure 2. Schematic view of Jominy test

The hardness is measured at intervals along its length beginning at the quenched end. For alloyed steels an interval of 1.5mm is commonly used where as with carbon steels an interval of 0.75mm is typically employed.

And finally the Rockwell hardness values are plotted versus distance from the quenched end.

The Jominy Test data illustrates the effect of alloying and microstructure on the hardenability of steels. Commonly used elements that affect the hardenability of steel are carbon, boron, Chromium, Manganese, Molybdenum, Silicon, and Nickel.

Carbon is primarily a hardening agent in steel, although to a small degree it also increases hardenability by slowing the formation of pearlite and ferrite. But this affect is too small to be used as a control factor for hardenability.

Boron can be an effective alloy for improving hardenability at levels as low as .0005%. Boron is most effective in steels of 0.25% Carbon or less. Boron combines readily with both Nitrogen and Oxygen and in so doing its effect on hardenability is sacrificed. Therefore Boron must remain in solution in order to be affective. Aluminum and Titanium are commonly added as "gettering" agents to react with the Oxygen and Nitrogen in preference to the Boron.

Slowing the phase transformation of austenite to ferrite and pearlite increases the hardenability of steels. Chromium, Molybdenum, Manganese, Silicon, Nickel and Vanadium all effect the hardenability of steels in this manner. Chromium, Molybdenum and Manganese being used most often.

4. Requested in the Test Report

-Draw Jominy curve for 1040, 1060, 4140 and 4340 steels depending on the distance from the end.

- Explain how the Grossman hardenability test is performed and the advantages and weaknesses compared to the Jominy experiment.

- Which mechanisms reduce the hardenability of steel when Al and Co are introduced? Explain.

- Which mechanisms increase the hardenability of steel when the other alloying elements except Al and Co are introduced? Explain.

- Why is the Jominy test not applied to high alloy steels? Explain.

5. CERAMIC RAW MATERIAL PREPARATION – REOLOGY

1. Purpose of the Experiment

The purpose of this experiment is to examine the basics of ceramic production and the preparation of a ceramic clay. Raw material preparation, grinding kinetics and rheological behavior of ceramic slurry will be studied in detail.

2. Theoretical Part

2.1. Preparation and Rheology of Ceramic Clay

A ceramic slurry contains ceramic raw materials, water and auxiliary substances such as binders, deflocculants etc. To prepare an optimum composition, special tables called Seger Tables or Seger Proportions are used. These Seger tables show the ratios between oxides in ceramic raw materials. It is necessary to keep the proportions constant when developing new compositions, because each oxide has a different effect on the rheology. Seger tables vary according to the final product and the properties required from the final product.

Rheology is the science of fluidity. It can be explained by two main values, fluidity, viscosity and thixotropy. Viscosity is the value of a material's fluidity. Fluidity and viscosity have an inverse ratio between them. Thixotropy is the change in viscosity over time.

There are two main fluid groups, Newtonian and non-Newtonian fluids. Newtonian fluids are like water, their viscosity does not change over time. However, for non-Newtonian fluids, viscosity changes over time. Viscosity of non-Newtonian fluids decreases with count time. Ceramic clay is a non-Newtonian fluid and shows thixotropic properties. For the rheological study of a ceramic slurry, terms such as flocculation, deflocculation and deflocculant should be explained. For ceramics, if the viscosity is too low, the surface quality of the products will be poor and there may be cracks on the surface. If the viscosity is too high, this will cause pinhole defects and difficulties for sludge handling (mobility).

Thixotropy is just as important as viscosity. If the thixotropy is too high, the drying time of the product will be longer. If the thixotropy is too low, it will cause the product to be fragile.

2.1.1. Flocculation, Deflocculation, Deflocculant

The particles of a clayey material suspended in water behave in two completely different mechanisms. This situation is caused by electrostatic charges on the surface of the particles that cause both pulling and repulsion.

Regularly, in an acid environment, the particles attract each other and this is called "flocculation". In an alkyl (basic) environment, the particles repel each other and this is called deflocculation.

In the case of deflocculation, the surface charges of the particles are neutralized, causing the particles to remain in suspension as individual discrete units. Without charges and without gravity, there is no force holding the particles together. Hence, there is a decrease in viscosity in the case of deflocculation. In the flocculation state, three-dimensional structures are formed due to electrostatic attraction between the particles. This leads to an increase in viscosity.

Deflocculant

Deflocculant term refers to an additive that causes a reduction in viscosity when added. Deflocculants prevent flocculation by increasing the zeta potential between particles, in other words, increasing the repulsive forces between particles.

There are several mechanisms for deflocculants to act in suspension. These;

-Basic addition or hydrolysis to raise the pH to basic values.

-The displacement of flocculant cations found together with the cations of the alkyl in double layer clays.

Adsorption of anions under electric field to obtain negative charge on particles.

Adding a protective colloid.

- Elimination of flocculating ions that may be present in the suspension by precipitation or the formation of coordination complexes.

Normally, the effects of deflocculants occur by the mechanisms mentioned above. Mechanisms do not depend on the nature of the deflocculant, which can be organic or inorganic.

3. Experimental Section

3.1. Required Tools

Mill, Viscometer, Mixer, Pyknometer, Sieve (90 µm), Drying Oven, Weighing Instrument.

3.2. Application of the Experiment

First of all, the raw materials are weighed and mixed according to the composition. Then the required amount of water and deflocculant are added to the mixture. Prepared sludge is ground in ball mills. After grinding, the density of the sludge is determined using a pycnometer. Regarding the density value of the sludge, a measurement is made by taking the weight corresponding to the density from the sludge. The prepared slurry is then mixed with a stirrer at 700 rpm and the viscosity value is determined using an analog viscometer with 20 rpm rotation speed. There should be a viscosity between 4-6 Poise (required value for floor tiles). If this value is not caught, a deflocculant is added to the sludge to fix the viscosity value. The amount of deflocculant added is determined by the rule of thumb. After each addition, the sludge is mixed for 3 minutes. is mixed and the viscosity value is determined using an analog viscometer with a rotation speed of 20 rpm. The viscosity value of the slurry is optimized between 4-6 Poise without adding extra water to stabilize the solids concentration. To determine thixotropy, after each viscosity measurement, the sludge is mixed for 5 min. rested. The viscosity is then measured again, the difference between these two viscosity values gives thixotropy. Once the stabilization of the viscosity is stabilized between 4-6 Poise, the addition of deflocculant is stopped. When the sludge reaches its final viscosity, the added deflocculant does not affect the viscosity until more deflocculant is added to the sludge. This high amount of added deflocculant does not behave as expected and increases the viscosity of the sludge. Thus, the proof of the achieved value of viscosity is the increase in viscosity with the added deflocculant in its stability and follow-up.

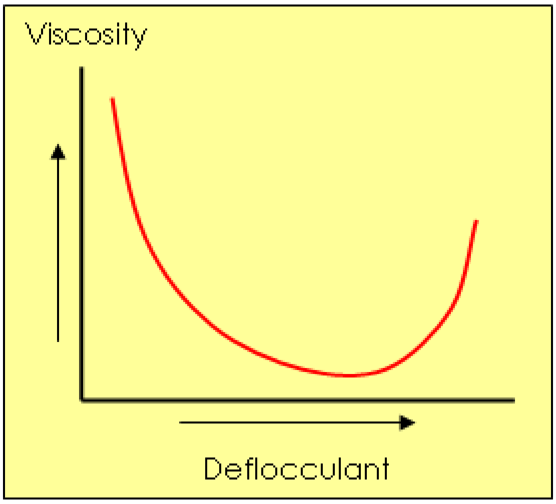

Figure 1. Viscosity-Added deflocculant diagram

4. Results

As a result, in this experiment, raw material preparation, grinding kinetics and rheological behavior of a ceramic slurry are explained and shown experimentally.

Resources

(1) RAHAMAN M. N., Ceramic Processing, 2006
(2) BARNES H. A., Handbook of Elementary Rheology, 2000
(3) WORRAL W. E., Ceramic Raw Materials, 1982
(4) CICEK B., Ceramic Processing Methods Lecture Notes, 2015

THERMOPLASTIC POLYMERS: SYNTHESIS OF POLYSTYRENE BY BULK POLYMERIZATION METHOD

Objective:

To investigate the effect of initiator concentration and temperature on bulk polymerization of styrene.

Theory:

Thermoplastic is a general concept used for polymers that can be reshaped by the effect of heat. Thermoplastics are the most commonly used polymers in making daily necessities and materials. Polyethylene (PE), polystyrene (PS), poly (vinyl chloride) (PVC) and polypropylene (PP) are the most widely used thermoplastics. These polymers are called basic plastics (general purpose, standard plastics).

Polystyrene (PS), one of the oldest known vinyl polymers; is hard, brittle, transparent, inexpensive, odorless and easy to process. Pure PS is also referred to as crystalline polystyrene, but this naming is not due to the high crystallinity of PS. It is rather due to the fact that the products made from this polymer are bright and transparent. In reality, PS is not crystalline, it is amorphous. Its glass transition temperature (T_g) is around 100 ^oC and it is suitable to use temperatures between -70 ^oC and 70 ^oC.

Molding methods such as extrusion, injection, vacuum forming, rotational molding are used to shape PS. Polymer processing temperature is around 180-200 ^oC, thermal deformation is observed at high temperatures. PS is resistant to aqueous solutions and bases, but soluble in many organic solvents. UV rays cause PS to decay. Electricity loss is low in all frequency and temperature regions. One of the weak points of PS is the low impact strength. In order to improve this feature; small fractions of elastomers (such as polybutadiene) are added into the polymerization medium during PS production and the polymer prepared in this way is called high impact polystyrene or anti-shock polystyrene.

Styrene has various copolymers such as styrene-acrylonitrile (SAN), styrene-maleic anhydride (SMA), styrene-butadiene (SBR) and styrene-acrylics as well as general purpose (crystal) and anti-shock homo-polymers. Thus, PS and its copolymers have a very broad and widespread use, from packaging to kitchenware, from toys to low voltage electronics, from synthetic resins to synthetic rubber, from the use of foam PS as sound and heat insulation material to the use of cross-linked polystyrene as ion-exchange resin (Figure 1).

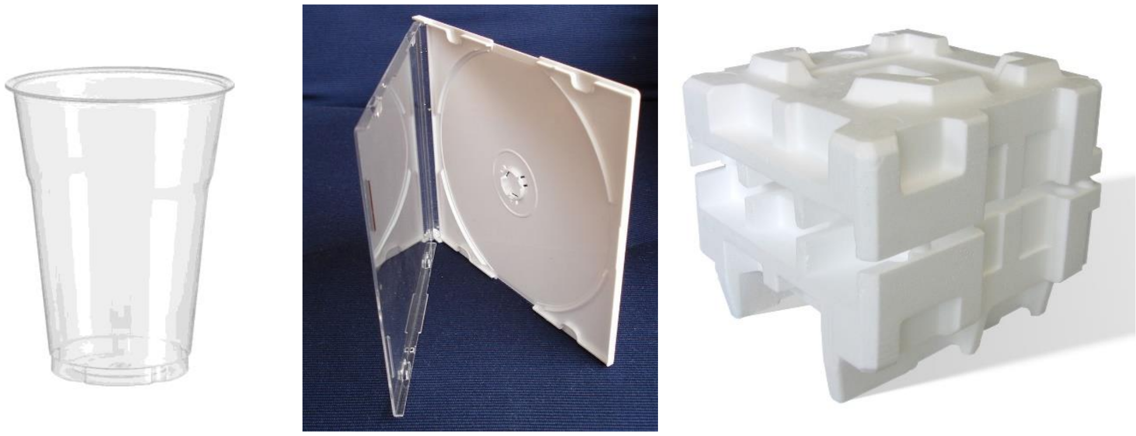

Figure 1: Various PS products.

Styrene polymerization is usually carried out via free radical mechanism; the polymerization initiator is thermally break into two pieces to form free active radicals. In order to initiate radical polymerization in the laboratory or industry, chemical compounds which can produce free radicals are often used. Solutions of chemicals like organic peroxides and azo compounds produce enough radicals for polymerization when they are heated to a certain temperature (Figure 2).

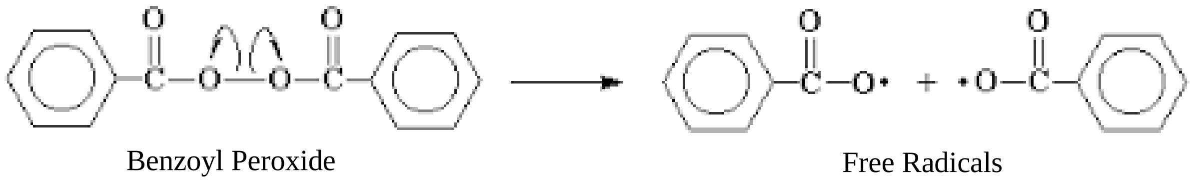

Figure 2: Benzoyl peroxide initiator thermally decomposes to form free radicals.

In the next stage, the active radicals combine with the styrene monomer to form a new, bigger radical; this new radical adds another monomer to itself; and through the addition of monomer after monomer, long polymeric chains occur in succession (Figure 3).

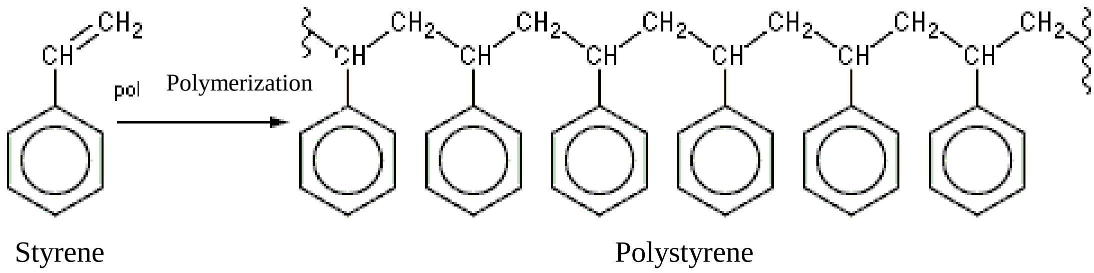

Figure 3: Formation of the polystyrene chain.

Styrene polymerization can be achieved by bulk, solution, emulsion and suspension methods. Bulk and suspension methods are generally used in commercial production of polystyrene. Bulk polymerization is a technique in which monomers are polymerized directly by initiators, heat and radiation. Bulk polymerization is superior to other polymerization techniques due to ease of application, economical efficiency, high polymerization rate, high conversion percentage, clean polymer production and allowing direct processing of the polymer. Polystyrene is one of the few addition polymers that are commercially produced on a large scale with bulk polymerization. It is possible to produce high-impact polystyrene, styrene-acrylonitrile resins, general-purpose (crystal-grade) polystyrene and various high-gloss, tensile-resistant polystyrene via this process.

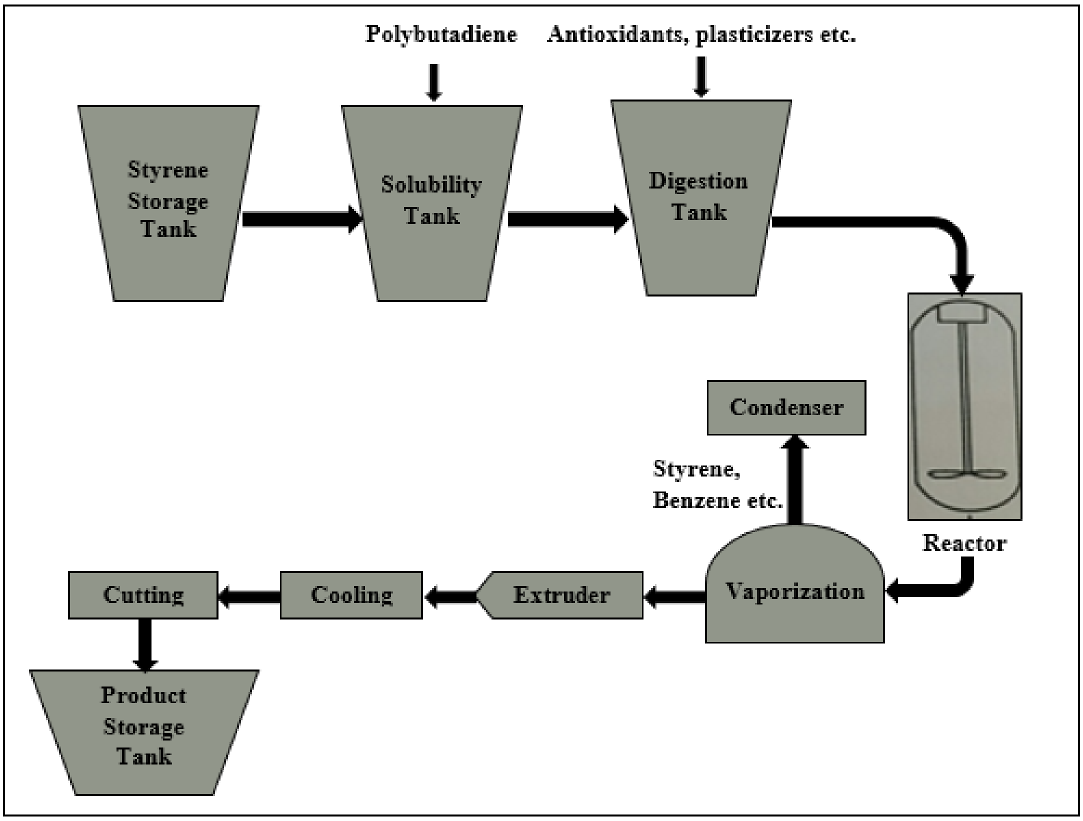

Figure 4: Flow chart of batch bulk polymerization of styrene.

Figure 4 shows the flow chart of production of high impact (anti-shock) polystyrene by batch bulk polymerization method. Pure styrene (together with other monomer if copolymer production desired) is taken from the storage tank into the solubility tank and then heated. Polybutadiene, which will increase the impact strength of the polystyrene, is introduced into the solubility tank in small pieces and dissolved in hot styrene by mixing. The mixture is then transferred from the solubility tank to a maturation tank into which additives such as antioxidants and plasticizers are added. It is followed by pre-polymerization. The partially polymerized mixture taken up in the batch reactor and then heated to sustain polymerization. Polymerization can also be initiated by placing a free radical initiator in the solubility tank. After the polymerization is complete, the molten polymer is pumped into a vacuum evaporator to remove styrene, impurities and oligomer structures that have not entered the reaction. The molten polymer is removed from the bottom of the vacuum evaporator and sent to the extruder. Cooled by passing through a water bath at the outlet of the extruder, then granulated and bagged (Figure 5).

(a) (b)

Figure 5: (a) General purpose crystal PS and (b) anti-shock PS.

Chemical materials and equipment to be used:

Monomer: Styrene

Initiator: Benzoyl peroxide (BPO)

Solvent: Benzene and methanol

Other materials: Test tube, beaker, heater, thermometer, pipette, pour, baguette, glass funnel, parafilm and filter (strainer) paper.

Experimental procedure:

1) Effect of initiator concentration on bulk polymerization of styrene: Number three test tubes as 1, 2 and 3. Weigh the selected polymerization initiator, benzoyl peroxide by the corresponding amounts of 1, 2 and 4 wt% of the monomer (2 g, m_1), respectively, and place in test tubes. Allow the initiator to dissolve by adding 2 grams of styrene to the test tubes. Cover the mouths of the test tubes with parafilm and pass nitrogen gas. After the nitrogen gas flow is finished, place the test tubes in a water tank at a constant temperature of 85 °C and let stand for 60 minutes. At the end of this period, remove the tubes and cool under the tap water. After cooling, measure the viscosity of the polymer solutions obtained from each tube. Open the mouth of the tubes and dilute the viscous solution with some solvent (benzene). Pour methanol to a beaker, about 15 times the amount of solvent you used. Add the diluted solution in the tube dropwise, stirring into the methanol. Do this for each tube separately. After the precipitation of the polymers is completed, filter the solution using a filter paper and dry the paper-retained polymers under vacuum. Weigh the synthesized polymers after drying is complete (m_2).

2) Effect of temperature on stack polymerization of styrene: Number three test tubes as 1, 2 and 3. Weigh the selected polymerization initiator, benzoyl peroxide in amounts corresponding to 1 wt% of the monomer (2 g, m_1) and place in the test tubes. Allow the initiator to dissolve by adding 2 grams of styrene to the test tubes. Cover the mouths of the test tubes with parafilm and pass nitrogen gas. After the nitrogen gas flow is finished, place 1st test tube in 80 °C, 2nd test tube in 90 °C and the 3rd test tube in 100 °C water tanks at constant temperature and let stand for 60 minutes. At the end of this period, remove the tubes and cool under the tap water. After cooling, measure the viscosity of the polymer solutions obtained from each tube. Open the mouth of the tubes and dilute the viscous solution with some solvent (benzene). Pour methanol to a beaker, about 15 times the amount of solvent you used. Add the diluted solution in the tube dropwise, stirring into the methanol. Do this for each tube separately. After the precipitation of the polymers is completed, filter the solution using a filter paper and dry the paper-retained polymers under vacuum. Weigh the polymers obtained after drying is completed (m_2).

Results and discussion:

1) Calculate the transformation % (polymerization %) amounts for each polymerization carried out in both steps by using Equation 1:

$$\text{Transformation \%} = \frac{m_2}{m_1} x100 \qquad (1),$$

Draw the transformation curve against the initiator concentration for the first experiment and the transformation curve against the temperature for the second experiment; determine curve behavior.

2) Using the viscosity values of the viscous polymer solutions obtained in the polymerizations you have performed, draw 2 separate charts for the viscosity against initiator concentration and the viscosity against temperature for the two test steps.
3) Interpret your observations and experimental results on these experiments in which you examine the effects of initiator concentration and temperature on the bulk polymerization of styrene and the properties of the polymer obtained.

SOL-GEL

The purpose of this experiment; to produce thin film coatings on ceramic based powders and substrates in nano sizes by using sol gel technique.

Sol gel method is a chemical process used in ceramic production. It was first discovered in the 1800s by Ebelman and Graham. From the 1930s on, Sol gel was widely studied and in 1938, the first patent on the sol gel process in Germany was obtained. In 1943, Jenaer GlasWerk made oxide coatings by sol gel method. When glass formation was achieved in room temperature in 1970s, it attracted attention again. The sol gel method comprises all systems in which a suspension can gel. In the sol gel method, the materials used in the production of high-tech ceramics are required to be sub-micron-size, pure reactive and sinterable at low temperatures. Nano-dimensional ceramic powder synthesis, thin-film ceramic coatings, ceramic-based materials and fibers can be produced by the sol gel method [1-3].

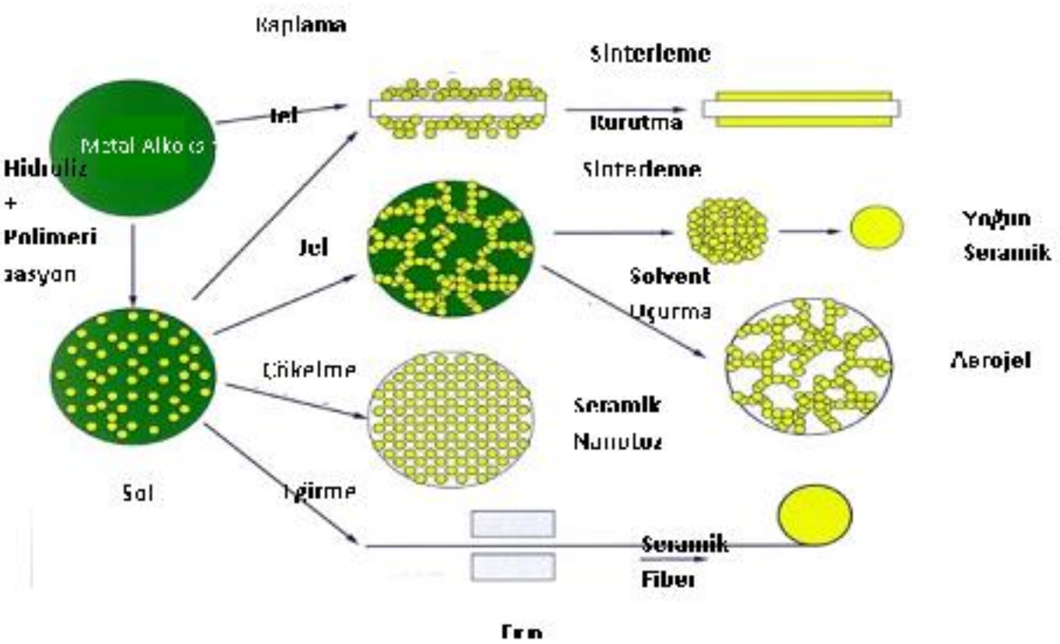

Figure 1. Sol Gel technology and products

What is Sol Gel?

The term sol gel defines the process of forming a three-dimensional solid particles (sol) and continuous network (gel) in the liquid after agglomeration of the nanoparticle solid particles dispersed in the liquid (1).

What is Colloid?

Colloid is a mixture of at least two different phases (solid, liquid or gas) in nano sizes. The colloid consists of a continuous phase and dispersion phases dispersed in this continuous phase. Continuous and dispersed phase combinations that may form colloids are listed below.

The liquid phase dispersed in the gas phase is also called aerosol. Example: Sis

Solid phase dispersed in gas phase: Example: Sooty or smoky weather

Gas phase dispersed in the liquid phase: Foams. Example: Shaving foam, whipped cream

The liquid phase dispersed in the liquid phase is called the emulsion. Example: Paints

The solid phase dispersed in the liquid phase is called Sol. Example: Dyes

The solid phase dispersed gas phase is called solid foams. Pomice stone, polystyrene foam

The solid phase dispersed liquid phase is called Gel. Gelatin, jelly

Solid phase dispersed solid phase is called solid left. Example: Color Glass

Unlike homogeneous solutions, the second phase added to the liquid in colloids is insoluble and there is a clear distinction between the two phases. The second phase can consist of nanoparticles and macromolecules. The dispersion phase dimensions vary from nanometer to micrometer [2].

What is sol?

The sol is the structure consisting of the continuous phase of the liquid and the dispersed phase of the solid. If the nano-sized solid particles dispersed in the liquid phase do not precipitate immediately, the structure is defined as the sol. It is possible to distribute the solid dispersed liquid phase in a homogeneous manner by external forces such as centrifugation.

What is Gel?

The gel is a solid-like and wet structure in which the nanoparticles forming the solid network structure are placed in 3D. Continuous phase in gel; the solid network formed by the nanoparticles, and the dispersed phase is the liquid phase. Gels have both solid and liquid properties. While their density is close to liquids, certain relationships exist between atoms, such as in solids.

Sol Production:

There are generally two methods of preparing the sol:

- Direct formation of nanoparticles in liquid: Molecules dissolved in the liquid are converted into larger molecules at the end of mixing liquids. The resulting macromolecules then become solid particles in nanoblocks. Example SiO2 (silica) based nanosol.
- Nanoparticles (such as carbon nanotubes and quantum points) are generated using specific production methods. The nanoparticles are then dissolved in the liquid phase. Surface modifiers (polymers, soaps, etc.) called surfactants are used to ensure homogeneous distribution.

Sol Gel Change:

For conversion of the solution to the gel, the solid nanoparticles dispersed in the solution must form a network structure. In order to form the network structure, the solid particles in the structure, called sal Brownian Motion çarp in the liquid, must collide with the molecules due to the effect of the heat and they must stick together at the end of the collision. The bonding process is much easier for solid particles with reactive groups on their surface. Because after the collision, reactive groups can form a bond. Since there will be no adhesion for solid particles with no reactive groups on their surfaces, the surfaces of such nanoparticles must be reactive with the additive or the surface to be reactive. As a result, non-reactive particles are bonded to the bond structure or electrostatic forces that will occur at the end of the collision.

As the solution turns into gel, the viscosity of the structure increases and the structure becomes non-flowable at the gel point. At the gelation point, the flow of the liquid has ended because the particles formed by the particles are dispersed within the entire volume of the liquid. After mixing the gelling agent into the solution, the duration is called süre gelling time kadar until the end of gel formation. [2].

Factors Affecting Sol Gel Chemistry:

Sol gel chemistry is affected by the following parameters.

- pH: pH is very important in colloid systems where water is involved. In the formation of silica gels, silanol groups are formed as a result of the hydrolysis of silica. The formation of silanol groups is affected by pH. The silanol groups then form the formation of the silica nanoparticles and the development of the web.
- Solvent liquid (solvent): It is very important that the nanoparticles do not precipitate during the formation of the nanoparticles. Therefore, the solvent must be capable of dissolving the nanoparticles. In addition, the solvent also helps the liquid nanoparticles to form the network structure, thereby guaranteeing gelation.
- Temperature: The kinetics of the formation of the nanoparticles and the formation of the network structure are activated by the temperature. When the temperature is too low, it increases the gelling time and causes too high agglomerates to over-grow and precipitate without forming the network structure.
- Heat Formed by the Reaction: Formation of the nanoparticles formed in the solution and the formation of the network structure, the heat released during the chemical reactions cause the reactions to accelerate.
- Time: Depending on the type of gel produced, gelation steps occur at different times. The properties of the product resulting from the slower-formed solution gel reaction are superior. The slower reaction is particularly uniform in the gelation stage. This allows higher strength and more transparent (transparant) gels (if desired). The more transparent gel structure appears less bluish because it causes less Rayleigh scattering.
- Catalyst: The solution is used as the acid (H +) and bases (OH-) catalyst in the gel technique. The solution gel method is sensitive to pH, as the catalytic effect is achieved by different mechanisms for acids and bases. Although the catalyst material is used in very small amounts (mg / mL), it reduces the gelation time from weeks to minutes.
- Mixing: The solution is important for mixing the solution in the gel technique, forming a chemical reaction in a uniform manner and for each molecule in solution to reach the chemical required for the reaction. However, after the gelling step has started, the continuation of mixing may lead to fragmentation of the semi-gelled web at micro and macro

levels. The gelling time is prolonged even if the gelation of the entire structure takes place at the end.

In sol gel application; inorganic compounds such as metal alkoxide solutions or metal powders, nitrates, hydroxide, oxides, etc. are combined with a certain proportion of water and acid to form a solution. By mixing the solution at certain temperatures, a series of chemical reactions occur in succession in the solution. A network is formed by the electrochemical interactions of the surface charges of the particles and this process is called gelation. This network is growing and reaching all points in the system to create a complete structure of the gel is obtained.[1-5]

Steps of Sol Gel Method

- Alkocyte hydrolysis

- Polymerization (Peptidization)

- Gel preparation

- Calcination and sintering

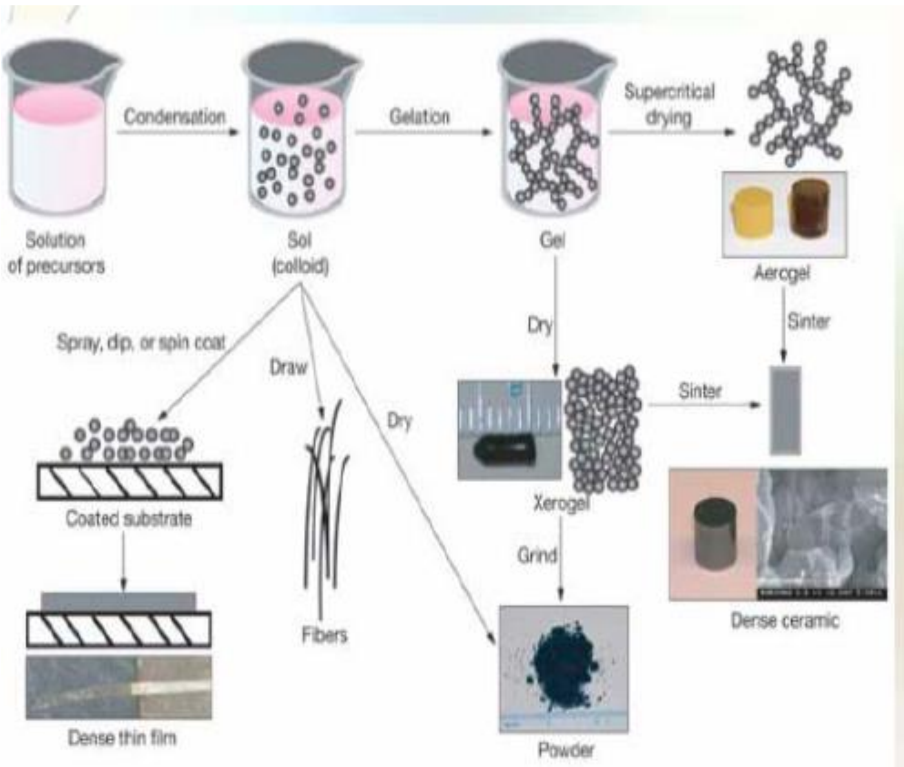

Figure 3. Sol gel steps [4].

The first step in sol gel synthesis is solution formation. In this step, various starting materials are mixed with the appropriate solvents to prepare homogeneous solutions. The sol gel process until the final product after the solution was prepared; hydrolysis, polymerization, gelation, and calcination / sintering.

I. Alkoxide Hydrolysis

Alkoxides are used as starting material to form a solution. M (OR) n.

- M; metal material to be coated,
- R; CH3 (methyl), C2H5 (ethyl) alkyl group,
- n; shows the values of the metal that vary according to the value.

Due to their high electronegative OR group, metal alkoxides exhibit high reactive properties. Physical properties are controlled by changing the alkali groups in OR. The amount of water, catalyst type, solvent concentration, temperature factors affect the rate of hydrolysis. Normally alkoxides are soluble in alcohol and hydrolyzed with water under acidic, basic or neutral conditions. The optimum molar water / alkoxide ratio is 100. When this ratio is obtained, the distance between alkoxide and water molecules increases. Acid catalysts bind polymers with light bonds while base (alkali) catalysts bind with strong bonds. When working in hot environment with distilled water (> 80 0C), a more stable colloid structure is formed [1, 5]. During the hydrolysis reaction, the OH-ion in the water replaces the OR-ion in alkoxide (Reaction 1).

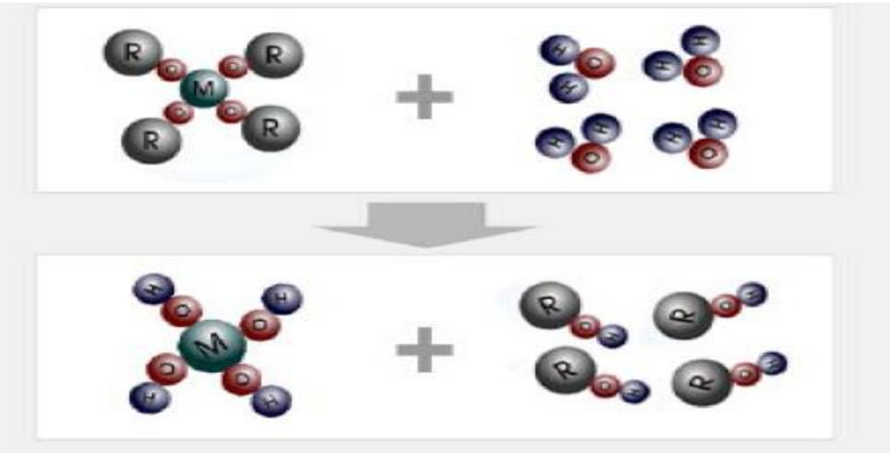

Figure 4. Alkoxide and hydrolyzed metal molecule

II. Polymerization (peptide):

The hydrolysed Si-OH molecules during the polymerization step form Si-O-Si (siloxane monomer) bonds with two different reactions (Reactions 2a and 2b). This process is defined as asyon condensation Bu. Condensation can take place in two ways: water condensation and alcohol condensation. In water condensation, water is released during the conversion of Si-OH molecules to Si-O-Si molecules (Reaction 2a), while alcohol condensation produces alcohol (Reaction 2b). The polymeric oxide structure is formed by hydrolysis and condensation reactions. The polymers in the solution grow with condensation reaction. This is the transition point from the solution to the gel and is determined by the increase in the viscosity of the solution.

In the polymerization process, the solution is prepared by dispersing the precipitates by a solvent action. The electrolytes used in the polymerization give the particles a certain charge. The reason for the loading is that the colloidal particles are stable only when they are loaded. The amount of acid to be used is adjusted by the pH of the medium [6]. Polymerization is a decoagulation event. (Coagulation is the collapse of the colloidal particles as a result of the zeroing of the electric charge.) If a solution forms a negatively charged colloidal solution, it forms a positively charged colloidal solution with OH yüklü ions (bases) and is polymerized with H + ions (acids). Peptidization does not occur if the electrolyte supplied to the solution is more or less than necessary. The high concentration electrolyte prevents the peptidization by leaving the grains unloaded. When it is used in small amounts, the sediment condition continues as the load is not sufficient [5-6]. The selected acid type is one of the important factors affecting peptidization. When the acid concentration is too low, the effect of the electric charge cannot be achieved. This condition makes it impossible to use almost all other organic acids in the solution gel process except for a few strong acids.

III. Gelation:

The monomers formed by the polymerization in the solution come together to form the nanoparticles [6]. The gelation event is closely related to the shape of the colloidal particles. The gel-forming molecules bind to each other with weak or strong bonds, forming skeletal tissues with liquid in the spaces between them. These tissues form the gel structure. The gel formation constitutes sufficient small sol particles for the prepared solution. These particles are formed by agglomerates (agglomerates) with the electrochemical interaction of the surface charges, or by the formation of gels of precipitated solid particles (Figure 5). The gels in this web structure are then spread over the entire structure and spread over three volumes of volume.

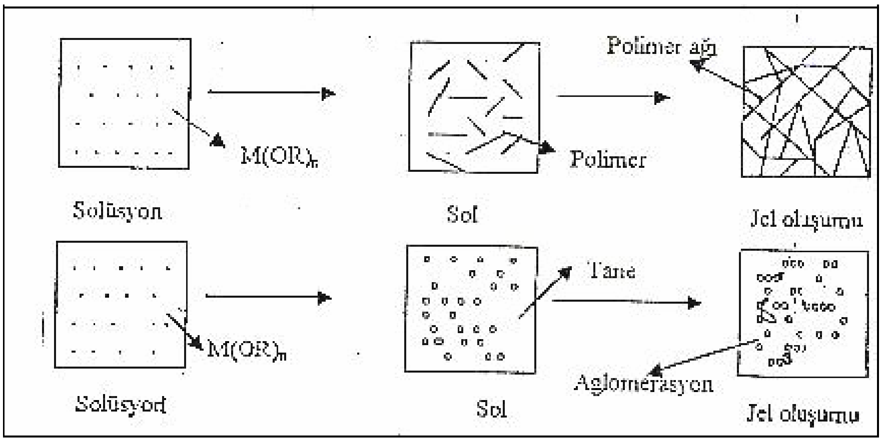

Figure 5. Polymerization Process

IV. Calcination and Sintering

After drying, the gel is heat treated for the production of dense ceramic material. According to the structure of the gel and the conditions of formation, the following reactions occur during the heat treatment;

• Decomposition of salts,

• Carbonization or waste organic combustion,

• Chemical water removal,

• Loss of micropores,

• condensation

The gelling structure is calcined by heating at a certain temperature without melting according to each material group. Gaps in the material are reduced in the material. With calcination and sintering, the mechanical properties of the material are also increased.

Advantages and Disadvantages of Sol Gel Method

Advantages of the Sol Gel method [3];

• Sintering of solids with high surface area and free energy at lower temperature is ensured.

• Fiber production is provided by the use of metal-alkoxide solutions (SiO_2, ZrO_2-SiO_2, Na_2OZr-SiO_2).

• It allows the production of solid glass materials which cannot be obtained by cooling from liquid phase (CaO-SiO_2, SrO-SiO_2, SiO_2-TiO_2, SiO_2-Al_2O_3).

• It allows the production of thin SiO_2 and TiO_2 (≤1µ) coatings on glass. Improvement of chemical, electrical and optical properties of coated surfaces is provided by sol-gel method.

• Controllable shapes and sizes of dust are produced (silica dusts).

• Homogeneous distribution of the second phases in the main phase (0.3% TiO_2-SnO_2)

Disadvantages [3];

• The cost of produced powders is high.

• The process is long and the amount of shrinkage during the process is high.

• Fine pores may be in structure.

• Residual hydroxide in the structure, residual carbon can be formed.

USED DEVICES AND MATERIALS

• Tetra Ethyl Ortho Silicate (TEOS, $Si(OC_2H_5)_4$)

• Ammonium Fluoride (NH_4F)

• Ammonium Hydroxide (ammonia, NH_4OH)

• Ethanol (C_2H_5OH)

•Pure water

• Fume hood

• Precision scales

• Magnetic stirrer

• Magnetic fish

• Pipette pump, pipette and dropper

• Beakers

• Materials for underlaying

•Turntable

•Power source

•Furnace

Experiment;

First, the solution is produced. When preparing the solution, mix the magnetic stirrer and the magnetic fish in a beaker of 5 mL ethanol (in a fume hood) with 3 mL of TEOS (solution I). (TEOS silicon based alkoxide is made by making it hydrolyzable in the lungs in case of inhalation and we recommend that the procedure be ventilated there.) Then 3 mL of water is dissolved in 5 mL ethanol (II. Solution). A solution of two different catalysts (Stock Solution) is used to form a solution. 1.9 g of ammonium fluoride salt (NH_4F) and 23 mL of ammonium hydroxide (NH_4OH) solution are dissolved in 100 mL of pure water for cleaning of the stock. 10 drops from stock solution II. It is added to the solution. Finally, I continued to mix I. Solution, II. The solution is slowly added to the solution. II. In the addition of the solution, the transparent is the whiteness of the solution and becomes opaque. This requires the growth of sold molecular molecular polymerization and the formation of nanoparticles. Since some of the light held in the preparation of the polymerization processor is planned through the nanoparticles (Tyndall Effect), the structure is opaque (milky). TEOS used in solution preparation; Si02 (silica) is the source, water; hydrolysis, ethanol; It is the solvent that helps TEOS and water to mix. The hydrolysis reaction activates the formation of Si-OH bonds by treating the base (alkali) based ammonium hydroxide (NH_4OH) as catalyst. Ammonium fluoride salt is used in case of not using hydrolysis, and fluoride ion in ammonium fluoride increases the reaction speed. As the polymerization treatment increases, the viscosity of the solution increases. In the case of paddles on the turntable, a dip coating process is carried out by turning the gel connections to the underlays on the turntable.

Dipping Coating:

The coating by dipping method is the process of dipping the lower material into a solution for coating the lower material and withdrawing it at constant speed, controlled temperature and atmospheric conditions.

Coating thickness;

• Lower material retracts

• Substrate surface tension

• Depends on the density and viscosity of the solution.

The steps of the coating by dipping method;

1. Dipping the substrate into the solution

2. Removing the substrate from the solution

3. Evaporation of the solvent from the solution on the surface of the substrate

Spin Coating:

Rotation The coating is used in the production of thin films. Typically the process is dripping the solution drop into the center of a base and then rotating the pad at high rotational speeds (typically 3000 rpm). Central acceleration results in the removal of excess solution and the dissolution of the remaining solution into the substrate surface.

Solution properties:

It depends.

• viscosity,

• drying rate,

• solid rate and

• with surface tensions

Terms of Transaction:

• speed,

• acceleration etc. Typically, the coating process consists of three steps.

1. Dropping solution on prepared substrate

2. With high-speed rotation, the removal and spread of excess solvent and

3. Drying of the solution by drying with gelation is completed by drying.

Powder Production with Gel Drying and Calcination:

Finally, the sol / gel poured into the mold is completely gelled at the end of 15 minutes. Drying of the gel (removal of water or alcohol as by-product) and calcination produce nanospheric SiO_2 powder. At the end of the calcination process, the powder obtained from the oven is ground in a mortar and the final powder product is obtained.

RECEIVING RESULTS

Weigh the gel product prior to drying and calcination. Re-weigh after drying and calcination. Thus, the weight loss in the sample is calculated as% Weight Loss.

At the end of the experiment gel production should be provided starting from the solution. The resulting gel must be dried and calcined with an oxide-based nanotope. The SiO_2 film should be formed on the substrates using immersion coating and rotation coating techniques of the prepared solution. The effect of these parameters on the coating quality should be observed by changing the active parameters (solution viscosity, coating speed, etc.) for both methods during coating. At the end of the experiment, the students will be able to:

1. Colloidal systems

2. Basic principles of sol gel technique

3. Sol Gel coatings

4. Characterization of coating layers

5. Sol Nano powder synthesis with gel technique

6. Preparation of the final report (theoretical knowledge, experimental study, results, references)

REFERANCES

1. http://www.aerogel.org
2. http://www.psrc.usm.edu/mauritz/solgel.html
3. Yrd.Doc. Dr. Atilla EVCİN, Sol Jel Prosesleri Ders Notları, *www2.aku.edu.tr/~evcin/*
4. James S. REED, Principles of Ceramics Prosessing, 2nd edition. 1995. Wiley Publishing, ISBN 978-0-471-59721-6
5. Pierro Alain C., 1998, Introduction to Sol Gel Processing.Springer Publishing, ISBN-978-0-7923-8121-1
6. John. D. Wright, Nico A. J. M. Sommerdijk, Sol Gel Materials Chemistry and Applications. Taylor and Francis Group, ISBN 978-90-5699-3269