



Metallurgical and Materials Engineering

Laboratory-II Booklet



T.C.

YILDIZ TECHNICAL UNIVERSITY

FACULTY OF CHEMICAL AND METALLURGICAL ENGINEERING

METALLURGICAL AND MATERIALS ENGINEERING

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LABORATORY-II

EXPERIMENT BOOKLET

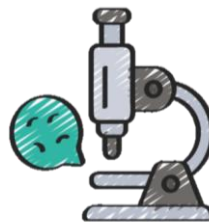
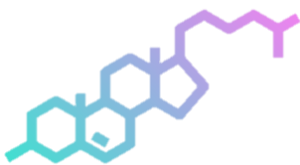




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SAFE WORKING PRINCIPLES IN LABORATORY

1. Handbags, coats, etc. should not be brought to the laboratory if possible. If these materials are brought to the laboratory, the materials should be kept at locations determined by the laboratory administrators.
2. During the application of laboratories, long hair should be tied up and pendant earrings and bracelets should be removed. If there are cuts, wounds, etc. on the hands, working in the laboratory is possible only after they have been covered with waterproof tape, peep toe shoes should not be worn in the laboratory.
3. Personal protective equipment (gloves, masks, eye / face protectors, hearing protection, work clothing) should be used to protect the eyes and the skin as long as worked in the laboratory.
4. No food and beverage should not be consumed in the laboratory, and the face should not be touched while working
5. It is necessary to know what is available in the first-aid chest and how the fire extinguisher works. Information about this must be obtained from the staff.
6. In the laboratory, movements that distract others should be avoided. Gaming or joking is strictly dangerous and forbidden in the laboratory.
7. Laboratory notebook should be kept for the studies conducted in the laboratory. Studies and observations must be recorded in this notebook.
8. Taps, gas valves and switches, should be kept closed when not in use.
9. Metallic laboratory tools should not be kept wet to avoid rusting.
10. The solid materials to be dispensed should be dropped into the designated waste bin in the laboratory.
11. Any incident occurred in the laboratory should be immediately notified to the administrators of the laboratory.
12. No substance or material should be taken out of the laboratory without the permission of the laboratory's administrators.
13. After use, each item should be cleaned according to the method of the appliance. Hands should be washed after leaving the laboratory.
14. Before using the microscope, the objective and ocular should be carefully cleaned with a cloth before and after each use without damaging the lens.
15. While diluting the acids and alkalis, they should always be poured slowly over the water, never the opposite.
16. If corrosive caustic substances such as acids or bases drip or splash to the naked skin, it should immediately be washed with plenty of water. The laboratory administrator must be informed about the incident.
17. When dealing with electricity, hands and electric switches and sockets must be dry. Electrical plugs should not be pulled out from the cord.



1. MINERAL PROCESSING (ORE DRESSING)

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.

THEORETICAL INFORMATION

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.

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; $0.1 \text{ mm} < \text{Grain Size} < 0.5 \text{ mm}$ and $\% \text{Fe}_2\text{O}_3 < 0.05\%$ are required.

Example 2. For iron ore used in pig iron production; $10 \text{ mm} < \text{Grain Size} < 100 \text{ mm}$ is required. For this purpose, crushing, grinding and sintering-pelletizing is applied. In addition, both $\% \text{P}$ and $\% \text{Na}_2\text{O} + \text{K}_2\text{O}$ must be $< 0.1\%$.

Example 3. In order to produce calcined magnesite or sinter magnesite at high quality from magnesite ore: $\text{SiO}_2 < 0.5 \%$ and $2 \text{ mm} < \text{Grain Size} < 30 \text{ mm}$ 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.

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.

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).

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

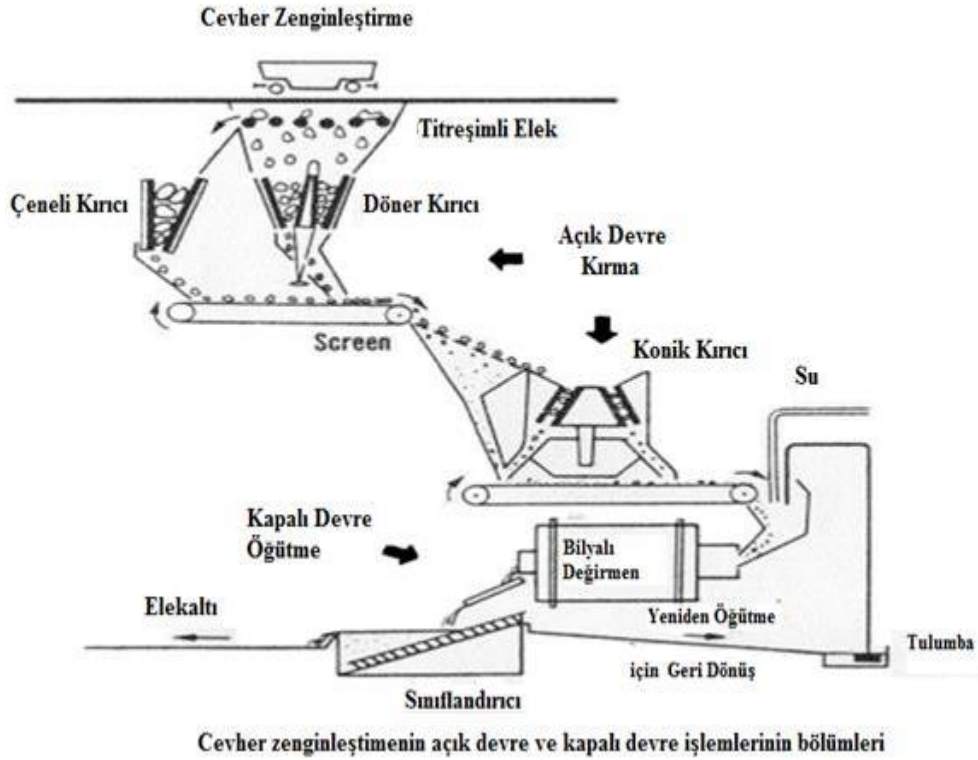


the material; different classifiers are used according to the applied process, structure of the ore, size, physical and chemical properties. These are known as; hydrocyclones, mechanical classifiers (spiral classifiers, notched classifiers, solid centrifugal classifiers) and air classifiers.

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.



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.

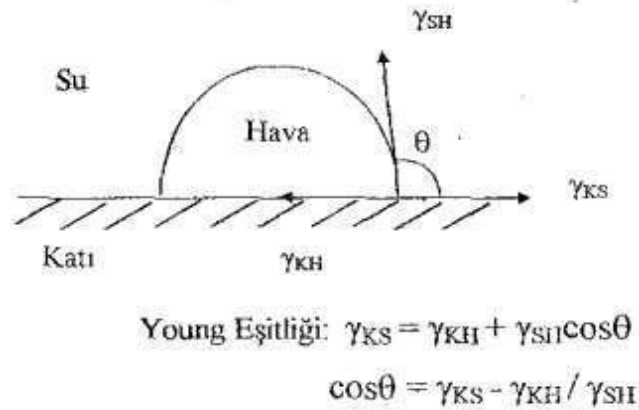


Figure 2. The forces in solid, liquid, air triple system and Young Equation

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 γ_c , 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 $\theta > 0$, 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 ($\gamma_c < 72$ dyn / cm) are wetted by surface-energized fluids lower than the Critical Wetting Surface Energy (γ_c). 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 ($\theta = 0$ 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 γ_c 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

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.

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- aerated 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, Humboldt, Massco.

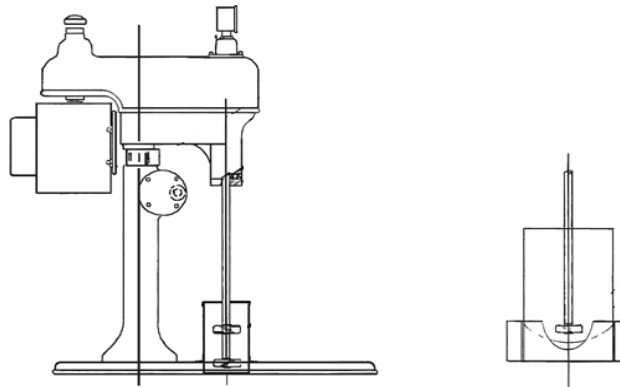


Figure 3. Denver flotation machine

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

EXPERIMENTAL PROCEDURE

1.1 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.

Flotation Experiment

- ✓ 200 g. of galena ore with $-200\ \mu\text{m}$ 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.

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).

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2. CASTING

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.

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.

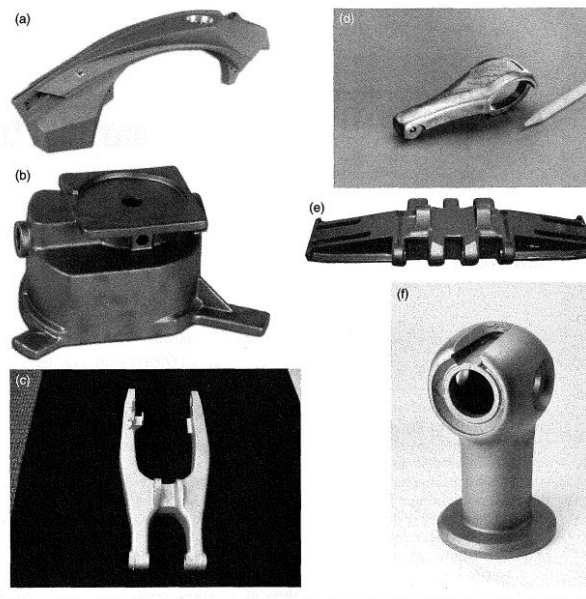


Figure 1 Typical castings in major alloys, (a) This motorcycle frame component was produced via the nobake sand casting process in 356 aluminum with T6 treatment temper, (b) The bronze alloy used for this dental suction pump was selected for its high strength, mechanical properties, and wear resistance, (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.



2.1 Advantages of Casting Process

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 economically 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.

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 in appropriate 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.

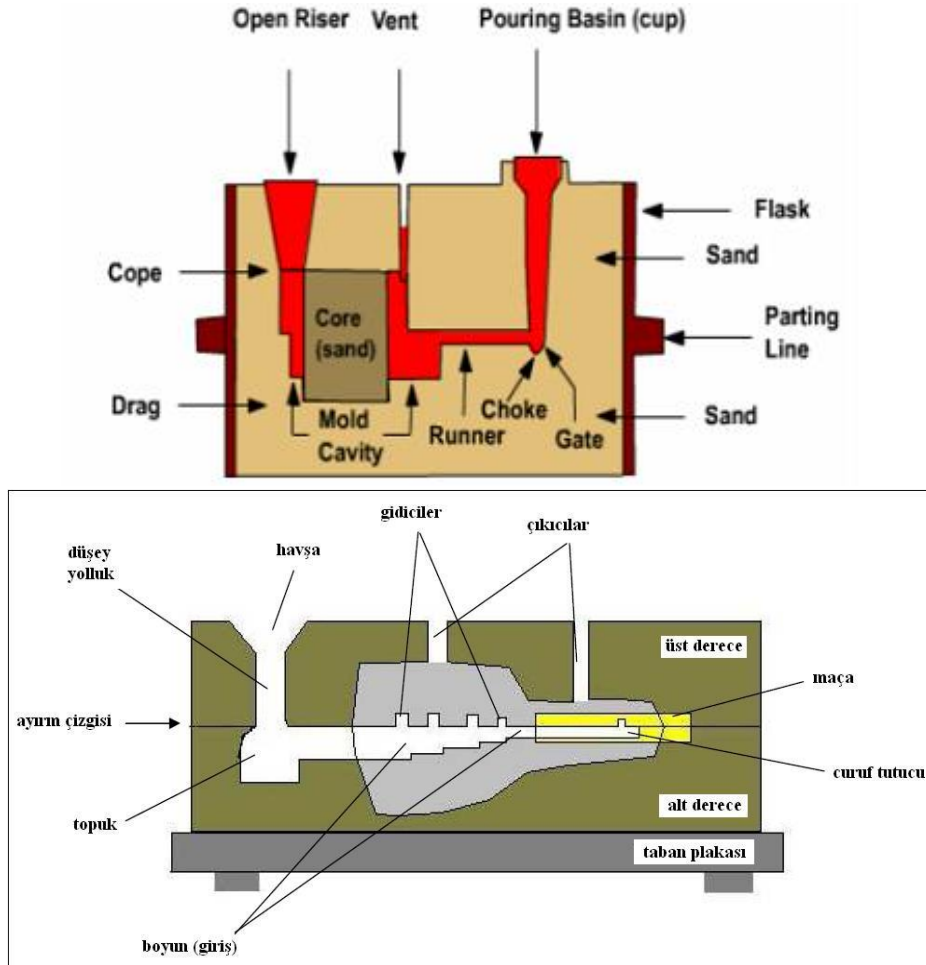


Figure 2 Mold section

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**

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.

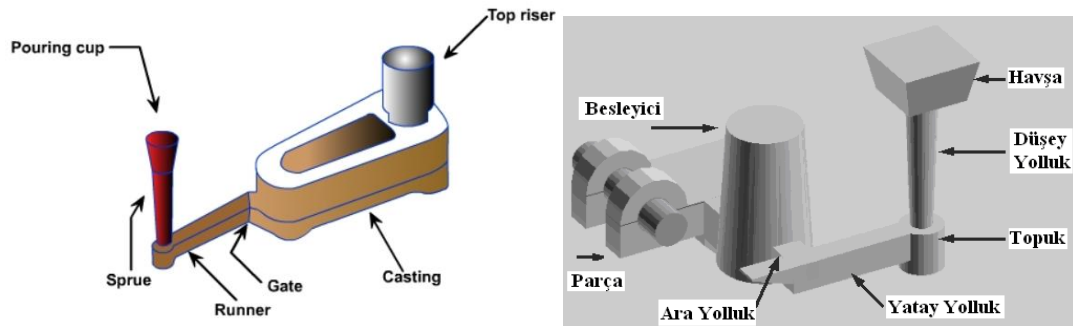


Figure 3 Pattern

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.

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.

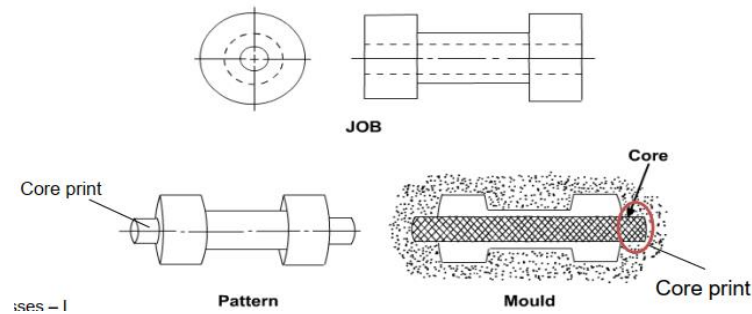


Figure 4 Core

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.

Molding

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

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.

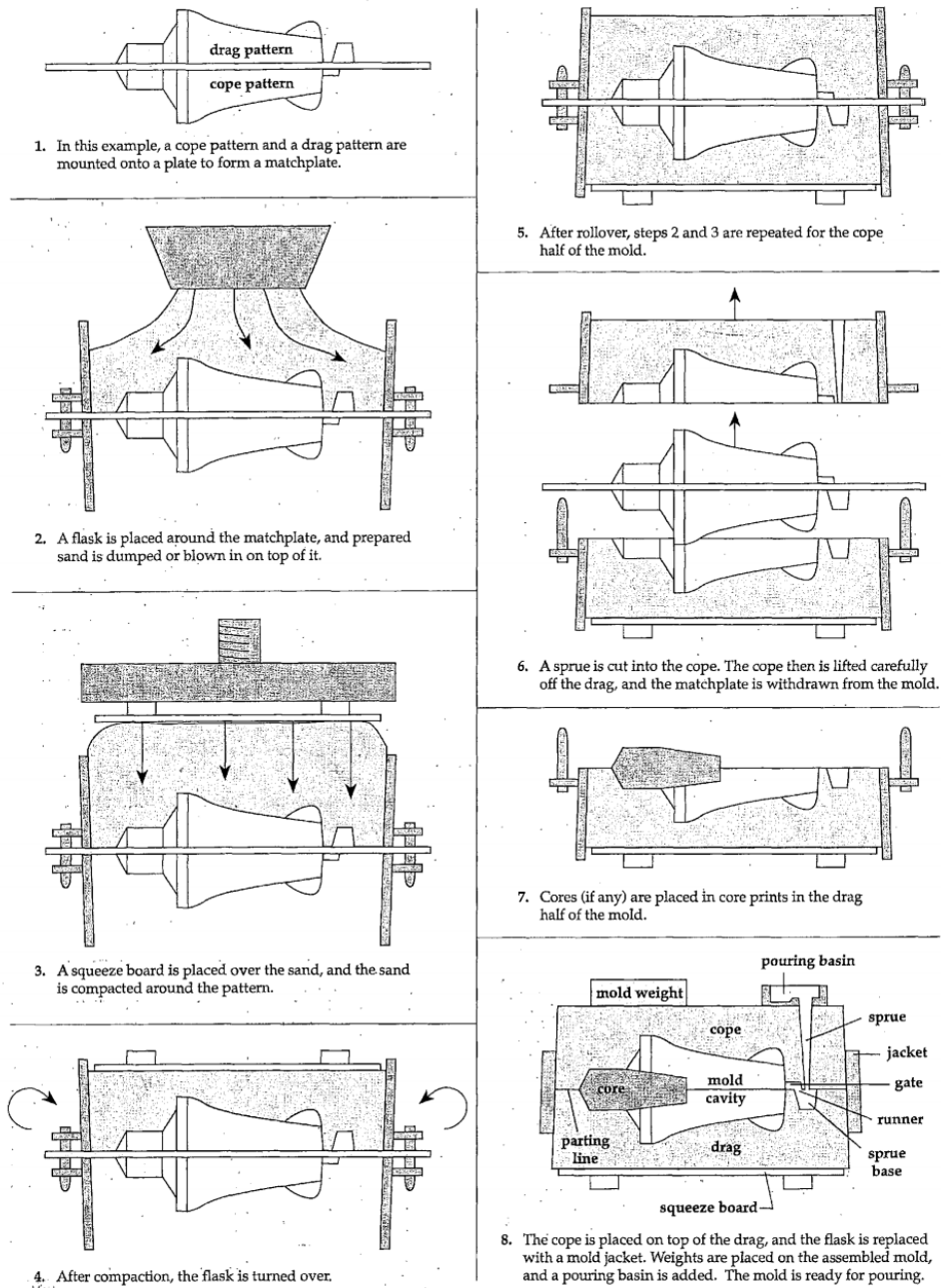


Figure 6 Steps of making sand mold

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 ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and bentonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$). 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 high.

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.



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 quality follows. The casting is then ready for shipment or further processing for example, heat-treatment, surface treatment, or machining.

Experimental Procedure

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.

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.

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3. 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.

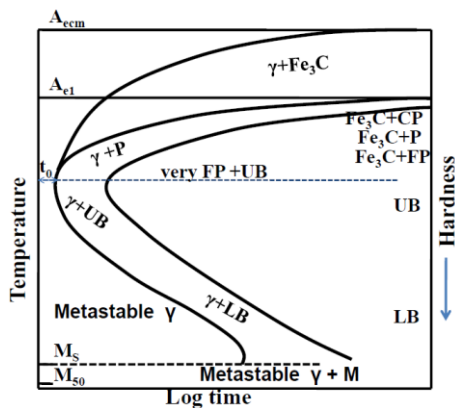
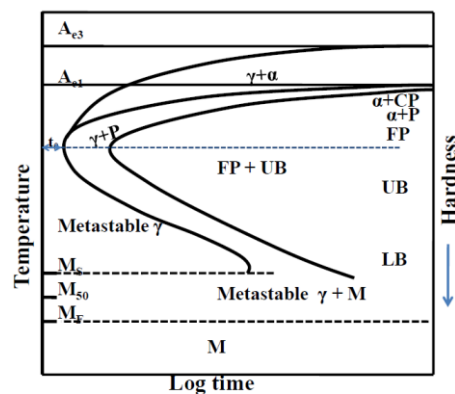
Almost all alloying elements (except, Al, Co) increases the stability of supercooled austenite and retard both proeutectoid and the pearlitic reaction and then shift TTT curves of start to



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.



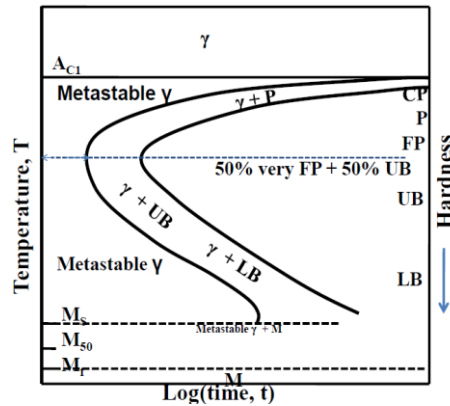


Figure 1. TTT diagrams for (a) hypoeutectoid, (b) eutectoid and (c) hypereutectoid steels

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.

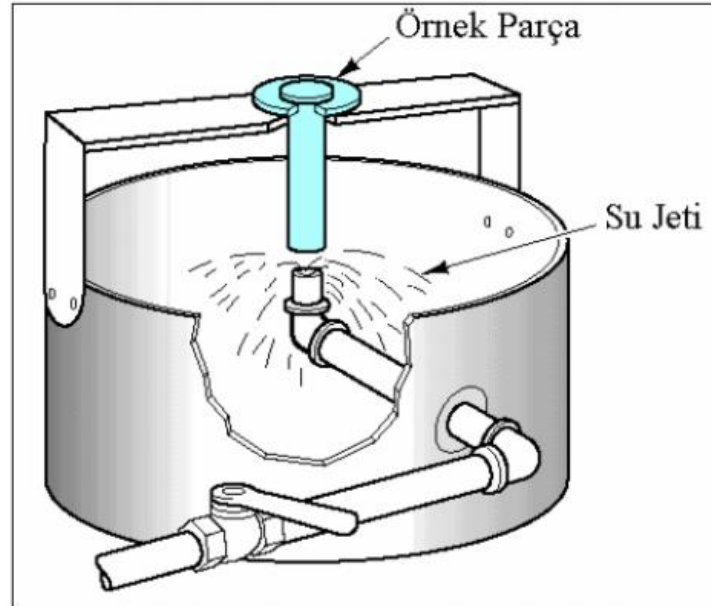


Figure 2. Schematic view of Jominy test

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.

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.

4. CHEMICAL ANALYSIS EXPERIMENTS

OPTICAL EMISSION SPECTROMETER

OBJECTIVE

Quantitative determination of the chemical content of metallic samples by using optical emission spectrometer.

THEORETICAL INFORMATION

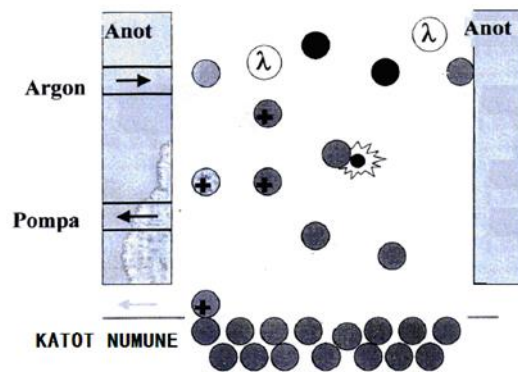


Figure 1. Sample – Gas Interaction

As shown in Figure 1, the gases in the cathode chamber are evacuated and argon gas is sent to this chamber with a pressure of 1-10 Torr. A high potential of 600-1500 Volts is applied. Thus, argon ions are accelerated towards the sample. At high temperatures generated by the stimulation of the sample, the electrons in the outermost orbit of the sample jump to a higher level orbital and on the way back, a radiation occurs because of the energy difference between the orbitals. This is called a spectrum. Each element has its own spectrum lines. This generated radiation is evaluated in the spectrometer.

In spectrometers which the optical sensors are used as photo tubes (with photo tube optical sensor), a separate measuring circuit and components are required for each element and a photo tube must be placed in the device for each desired element. This not only significantly increases the size of the device, but also limits the number of elements to be analysed. A further



difficulty is the need for a vacuum system and a room with air conditioning for this kind of spectrometers.

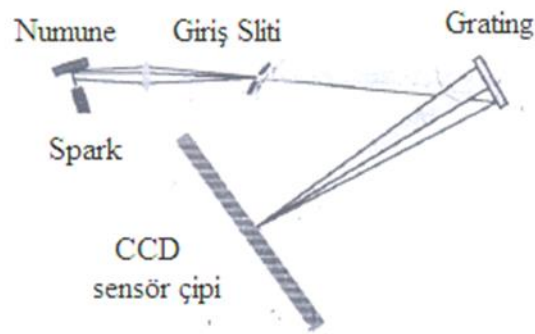


Figure 2. OES with single CCD system

With the CCD optical sensor spectrometer technology, all these problems were overcome by using a detector measuring the entire elemental spectrum in the selected range (Figure 2). By providing argon gas to the optical chamber, an inert environment can be created and low wavelength elements can be monitored. In this system, multi-based analysis can be done in a natural environment easily and quickly, without requiring special equipment such as vacuum, air conditioning and any additional parts. In a separate system, entire spectrum can be traced without any loss, by placing CCD chips on the Rowland circle and increasing the number of detectors (Figure 3).

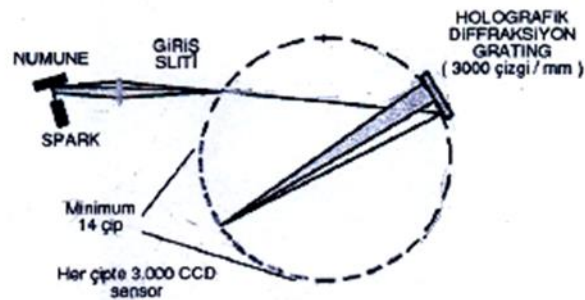




Figure 3. OES with multi CCD system

Components of atomic absorption spectrometry:

- ✓ Light source, emitting light that will be absorbed by the element to be analysed
- ✓ Atomizer, where the sample solution becomes atomic vapor
- ✓ Monochromator, for separating the working wavelength from other wavelengths
- ✓ Detector, for measuring light intensity

WORKING PRINCIPLES OF PHOTO-TUBE SYSTEMS

If the sample is heated between two different electrodes by means of electrical current, atoms emit lights at their specific wavelengths. This light comes into the spectrograph from a narrow gap. With the help of the prisms and lenses here, the light, separates into different wavelengths and falls on the photographic film so the lines on the photographic film belong to the lights emitted by certain elements.

WORKING PRINCIPLE OF DETECTOR SYSTEMS

In the ignition zone, a spark discharge occurs between the tungsten electrode and the lower surface of the sample, whereby the spectrum is obtained. The resulting spectrum focuses from the input gap into the mirror and here the light (spectrum) is decomposed into its wavelengths by spectral scattering. The amount of elements corresponding to certain wavelength ranges is determined by the detector in the chamber in an atmosphere of continuous argon gas.

DEVICES AND MATERIALS USED

- ✓ Sanding machine
- ✓ Optical emission spectrometer
- ✓ Sample to be analysed
- ✓ Reference sample
- ✓ Sandpapers



EXPERIMENTAL PROCEDURE

Sample Preparation: The surface of the sample to be examined must be smooth. The surface is sanded with a sandpaper of 60. The surface of the reference sample is also sanded.

Analysis: The reference sample is chosen according to the type of specimen to be examined. The reference sample is placed in the combustion chamber. Incineration is done several times in order to understand if burning is successful. If the image obtained by the combustion process is satisfactory, the device is calibrated accordingly. When the calibration process is finished, the reference sample is analysed. If the analysis results match the standard values of the reference sample, the analysis of the sample starts. If the sample is smaller than the combustion chamber, it is covered with putty. A wire-shaped adapter is placed and the combustion process is performed. The reference name is entered according to the type of sample. Combustion process is applied to the sample three times. The average of the three results is used.

OBTAINING RESULTS

The result of the analysis of the reference sample is compared to the standards. The average value of the analysis of the sample to be examined are compared with the standards. The values that are closest to the values in the standards are taken. Thus, quantitative analysis of the material is determined.

2. ATOMIC ABSORPTION SPECTROMETER

OBJECTIVE OF THE EXPERIMENT

Determination of the elemental composition of metals belonging to different types of alloys using Atomic Absorption Spectrometer (AAS) device.

THEORETICAL INFORMATION

A sample of each element in the vapour phase gives a distinctive line spectrum when excited. Therefore, spectroscopy is a very functional method to analyse (determine) the composition of an unknown substance.



Flame spectroscopy is a branch of spectroscopy based on free atoms. The substance is heated in a flame to obtain free atoms. For this, the inorganic substance that has been brought into solution is formed into very small globules in a special mechanism and sprayed into the flame. Inorganic matter dissociates into atoms at this temperature.

Atomic absorption spectroscopy is the branch of spectroscopy, which is founded on the partial absorption of a specific wavelength beam of light sent into the flame from another source by an atom in a flame and measuring the degree of decrease of the remaining characteristic beam, and the device in which this measurement is made is called FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER.

The light sources used in atomic absorption spectrometry are:

- 1) Hollow cathode lamps (HCL)
- 2) Multi-element lamps
- 3) Electrodeless discharge lamps (EDL)
- 4) High luminous lamps

HOLLOW CATHODE LAMPS (HCL)

It is the most widely used light source in atomic absorption spectroscopy. It consists of a cylindrical glass lamp filled with Ar or Ne at 1-5 pressure, containing a cathode and an anode. The cathode is made of a very pure metal of the element under study or an alloy containing that element. The anode is usually a tungsten or nickel wire. Hollow cathode lamps require separate lamps for each element. A current of 1-50 mA is created by applying sufficient voltage between the electrodes. With this voltage, the inert gas ionizes at the anode and is pulled towards the cathode at a high speed and strikes the cathode, forming a cloud of metal atoms. Then excited metal atoms are obtained by collisions with free atoms. They radiate the characteristic spectrum of the cathode element as they transition to the ground state.

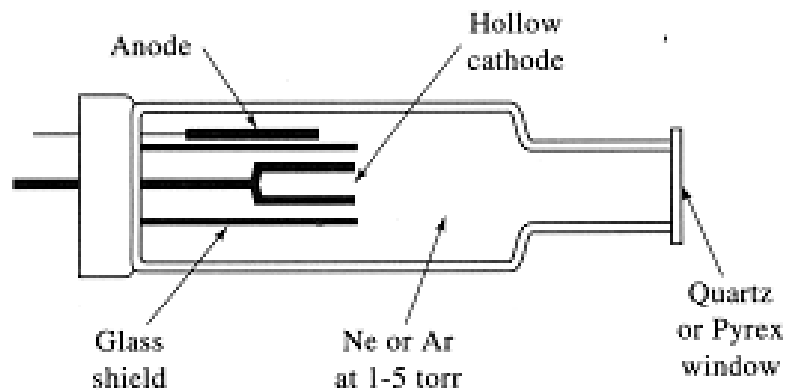


Figure 4. Schematic representation of the hollow cathode lamp used in the Atomic Absorption Spectrometer instrument

Flame atomic absorption spectrophotometer is an important tool used in elemental analysis. The elements sought in the sample are found with the help of the absorption of light at the wavelength specific to that element. In the cathode lamp, since the wavelength of the sought element is generally obtained by excitation of the element itself, it can give very sensitive results for the amounts in the sample. It is generally used for metals.

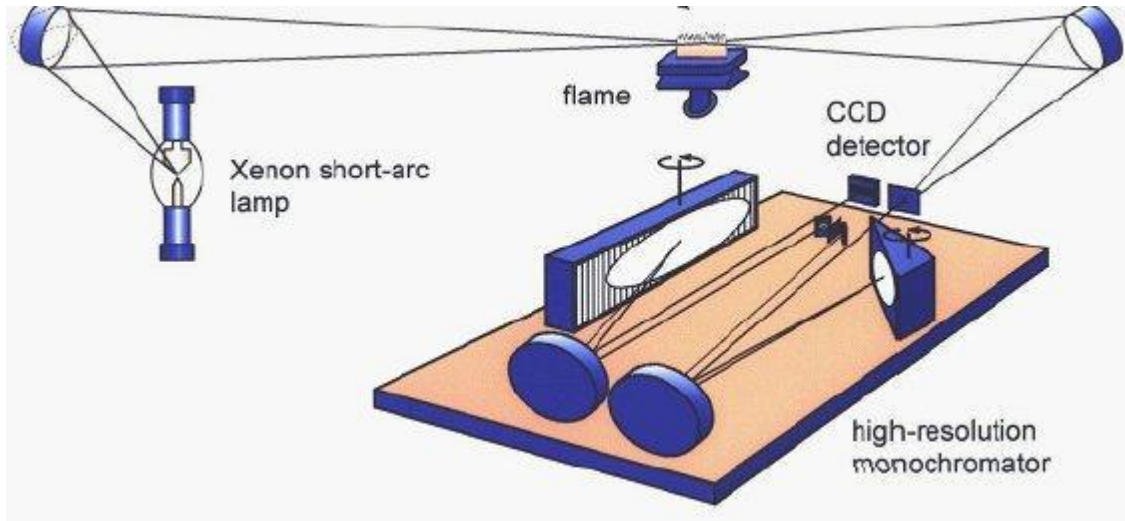


Figure 5. Schematic representation of Atomic Absorption Spectrometer

In the atomic absorption spectrometer setup, the beam emanating from the light source passes through the flaming section where absorption takes place. The absorbed beam is evaluated in the so-called monochromator (by measuring the absorbance), and the necessary data is transferred to the electronic system or the lever indicator as data. The system consists of a simple mechanism as seen.

- 1) The solution to be analyzed is given to the system through a thin hose.
- 2) The sample solution is drawn by the engine and sprayed on the flaming part in the form of mist.
- 3) This is the part where the sample is atomized and the beam is absorbed by the sample atoms. The gas that will form the flame is chosen according to the heat required for the sample to atomize.

FLAMING SECTION



We should choose the fuel we will use in the atomic absorption spectrometer according to the element to be atomized. Mainly used fuels are **Acetylene, Hydrogen, Propane, Butane** and **Natural Gas**.

In atomic absorption spectrometer, oxygen, nitrous oxide, air, air + oxygen are used as combustible gas. A mixture of acetylene and nitrous oxide ignites at very high temperatures. Since alkali metals give stable oxides, their determination is made in acetylene-air mixture. However, they dissociate to some ions in the acetylene-air mixture. On the other hand, since the oxides of elements such as lead, copper and zinc are not durable, even a natural gas-air mixture may be sufficient for their determination.

Events Occurring in Flame Temperature:

- ✓ Sample dries at high temperature.
- ✓ The salts in the dried sample turn into gas molecules.
- ✓ Gaseous salt molecules decompose to give free element atoms.
- ✓ Some of the free element atoms in the flame heat up to the excitation temperature.



5. 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 (5 μm , 1 μm 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.

<u>Stage</u>	<u>Abrasive</u>	<u>Lubricant</u>	<u>Cloth</u>
Rough Grinding	Silicon Carbide	Tap Water	
Fine Grinding	Grit 240		
	Grit 320		
	Grit 400		
	Grit 600		
Rough Polishing	Gamma Alumina 1.0 μ	Tap Water	Rayon
Final Polishing	Gamma Alumina 0.05 μ	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 re-etching 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 Hydrochloric 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.



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:

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

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** = $1/(N M)^{1/2}$

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.

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 $5\mu m$ and then with $1\mu m$ and then proceed to $0.05\mu m$ 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% Nital (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 underetch 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.

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6. INVESTIGATION OF OPTICAL PROPERTIES OF MATERIALS

OBJECTIVE: The objective of this experiment is to:

- A. measure the transmittance of ultraviolet and visible radiation by a set of standards optical materials.
- B. observe the transmittance of visible and ultraviolet radiation by optical materials and see the amount of radiation blocked out by these samples.

MATERIALS AND EQUIPMENT:

UV–Vis spectrophotometer, standard optical materials, alcohol, deionized water, drying paper

THEORETICAL BACKGROUND:

Spectroscopy is the study of objects based on the spectrum of color they emit or reflect. Scientists spend much time studying the interactions between matter and energy. Because there are several forms of energy and a large supply of matter, these studies have provided many measurements and much knowledge about the universe and its behavior. A study of electromagnetic energy with matter provides valuable and important information about molecular structure and properties. In fact, some of the most convincing evidence about atomic and molecular structure, and the origin and makeup of the universe have been obtained this way.

Light is electromagnetic radiant energy. Depending upon the point of view, light can be thought of as having either wave properties or particle properties. The argument as to whether light behaves as waves or particles persisted for centuries. Wave–particle duality is a theory that proposes that all matter exhibits the properties of not only particles, which have mass, but also waves, which transfer energy. A central concept of quantum mechanics, this duality addresses the inability of classical concepts like "particle" and "wave" to fully describe the behavior of quantum-scale objects. The idea of duality originated in a debate over the nature of light and matter that dates back to the 17th century, when Christiaan Huygens and Isaac Newton proposed competing theories of light: light was thought either to consist of waves (Huygens) or of particles (Newton). Through the work of Max Planck, Albert Einstein, Louis de Broglie, Arthur Compton, Niels Bohr, and many others, current scientific theory holds that all particles also have a wave nature (and vice versa). According to the wave theory, electromagnetic radiation is composed of both



electric and magnetic fields whose waves vibrate in mutually perpendicular planes. It is the electric field of light interacting with the electrons of matter which produces observable properties of a substance. Two fundamental characteristics are associated with any wave – the wavelength and the frequency. The wavelength, λ (Greek letter, lambda), is measured from the crest of a wave to the adjacent crest (see Fig. 1). Wavelengths range from very small (measured in nanometers, 10^{-9} m) to quite large, several meters. The frequency is the number of waves passing a point in unit time and is designated ν (Greek letter, nu). Frequency can be expressed in cycles (or vibrations) per second. Wavelength and frequency are inversely proportional to each other; the shorter the wavelength, the more waves pass a point in a given time and thus the higher the frequency. Similarly, the longer the wavelength, the lower the frequency.

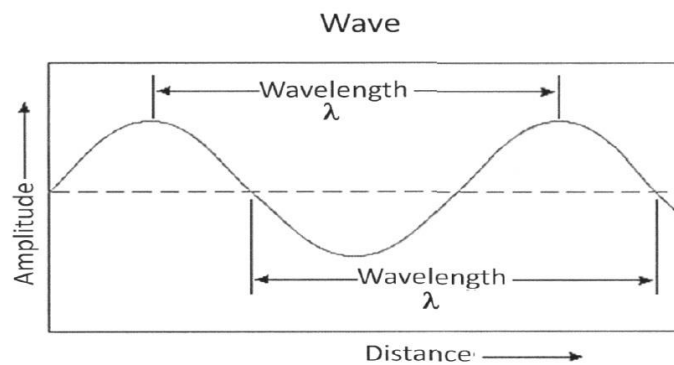


Fig. 1: The description of wavelength

Wavelength and frequency are related by the speed of light ($c = 2.998 \times 10^{10}$ cm/sec).

$$c = \lambda \nu$$

Another important relationship is that between these quantities and the energy of light.

$$E = h\nu \text{ or the equivalent } E = hc / \lambda$$

Where: h is Planck's constant (6.626×10^{-34} Joule.sec)

The greater the energy of the radiation, the shorter its wavelength and the higher its frequency; the smaller the energy of radiation, the longer its wavelength and the lower its frequency.

Relationship of Light Absorbed or Transmitted and Observed Color



Light from the sun is composed of a continuum of energies and thus, of a continuum of wavelengths and frequencies. Most of the electromagnetic radiation continuum is invisible to humans; the portion we perceive is referred to as visible light. Wavelengths of visible light extend from about 800 nm (8.0×10^{-5} cm) to about 400 nm (4.0×10^{-5} cm). Fig. 2 shows the entire wavelength range of the electromagnetic spectrum arbitrarily divided into regions called bands and the portion occupied by visible light.

It is against the high energy Ultraviolet (UV) radiation that sunscreen lotions are formulated to protect our skin in the outdoors. Our skin perceives the low energy infrared (IR) radiation only as heat. The lamps placed over food in cafeterias emit most of their energy in the red part of the Infrared region, keeping the food warm.

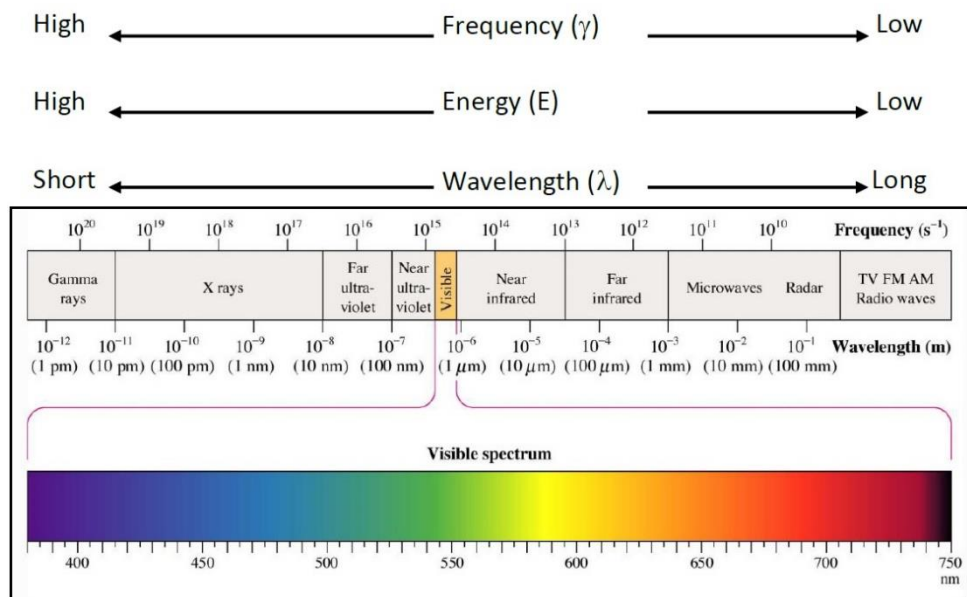


Fig. 2: Electromagnetic Spectrum

If little or none of the visible light striking our eyes is not absorbed prior to striking the eye, the color appears white. If this band of visible light is separated into narrow bands of wavelengths by a prism, we perceive the component colors. Isaac Newton divided the visible spectrum into seven color bands ranging in sequence starting with the shortest wavelengths (left to right in Fig. 2 above): violet, indigo, blue, green, yellow, orange, red.



When light impinges on a substance, one or more combination of things can happen to the light. The light can be scattered, reflected, transmitted, or absorbed by the substance. The absorbed light energy causes such changes as atomic and molecular rotation, vibrations, and electron transitions to higher energy levels. As a result of this absorption, our eyes or specially designed instruments may sense phenomena such as heat, fluorescence, phosphorescence, or color. Modern instrumentation can record these phenomena to a very high degree of precision.

The simplest cases are those where all incident light directed at a substance is either absorbed or transmitted. If a substance absorbs all wavelengths in the visible range, none of the light is reflected back to our eyes and the substance appears black. If the substance absorbs none of the incident visible light, it appears white (all light reflected) or colorless (all light transmitted). Colorless substances usually absorb in the UV or IR regions of the spectrum, on either side of the visible range.

Table 1: The wavelengths of colors observed, and colors absorbed

Wavelength Absorbed (nm)	Color Absorbed	Color Observed
410	violet	yellow-green
430	blue-violet	yellow
480	blue	orange
500	blue-green	red
530	green	purple
560	yellow-green	violet
580	yellow	blue-violet
610	orange	blue
680	red	blue-green
720	red-purple	green

If a substance absorbs light principally in one wavelength range (generally, a number of wavelengths on both sides of the principal absorption are also absorbed, so a broad absorption band results), the color perceived will be a mixture of all the wavelengths which are not absorbed. For example, the indigo dye in blue jeans has its maximum absorbance in the 500 – 650 nm range. Because this absorbance is in the red-to-green region, the wavelengths which are not absorbed are in the 400-500 nm range, thus, the color observed would be blue-violet. An aqueous solution that appears yellow, a narrow range around 550 nm, means that wavelengths on either side of yellow, primarily blues, greens and reds, are being absorbed. A green solution would be expected to transmit green wavelengths, while blocking blues,



yellows, and reds. Table 1 is a summary of the relationship between the wavelengths of colors observed and colors absorbed.

Complementary Colors:

A more fundamental grouping than Newton's are the systems of 3 primary colors and their secondary complementary colors. Complementary colors are pairs of colors which, when combined in the right proportions, produce white or black. When placed next to each other, they create the strongest contrast and reinforce each other. They are widely used in art and design and especially in video monitors, such as television screens. In painting, which uses subtractive colors, the traditional primary-secondary complementary color pairs, described since at least the early 18th century, were red-green, yellow-violet, and blue-orange. The more accurate RGB (red, green, blue) color model, invented in the 19th century and fully developed in the 20th century, uses additive color combinations of red, green, and blue light against a black background to make the colors seen on video screens. In the RGB color model, the light of two complementary colors, such as red and cyan, combined at full intensity, will make white light, since two complementary colors contain light with the full range of the spectrum. If any of these three colors is absorbed from white light, the complementary color is observed. The proper combination and intensities of the three primary colors create every conceivable color and shade. Table 2 below is a summary of the primary-secondary complimentary colors used in the RGB model.

Table 2: Primary and Secondary Complementary Colors

Complimentary Colors and Wavelengths of Maximum Absorption (nm)				
Primary			Secondary	
Red	690	↔	Cyan (Green-Blue)	488
Green	520	↔	Magenta (Red-Blue)	(non-spectral)
Blue	480	↔	Yellow (Red-Green)	580

Spectroscopy:



Spectroscopy is a basic analytical technique and research tool that utilizes the interaction between matter and electromagnetic energy. A spectrometer is an instrument that separates electromagnetic radiation according into wavelengths, passes these separated wavelength bands through a sample, and detects the intensity of the transmitted light. In analyzing a new sample, a scientist first determines the sample's absorbance spectrum. The absorbance spectrum is a plot of absorbance vs wavelength and shows how the absorbance of light depends upon the wavelength of the light.

The absorption spectrum is characterized by the wavelength of maximum absorption (λ_{max}) at which the absorbance is the greatest (see Fig. 3 below. The value of λ_{max} is important for several reasons. It is used in order to obtain the highest sensitivity and to minimize deviations from Beer's Law (see development below). It is characteristic of each unique compound providing information on the electronic structure of the compound.

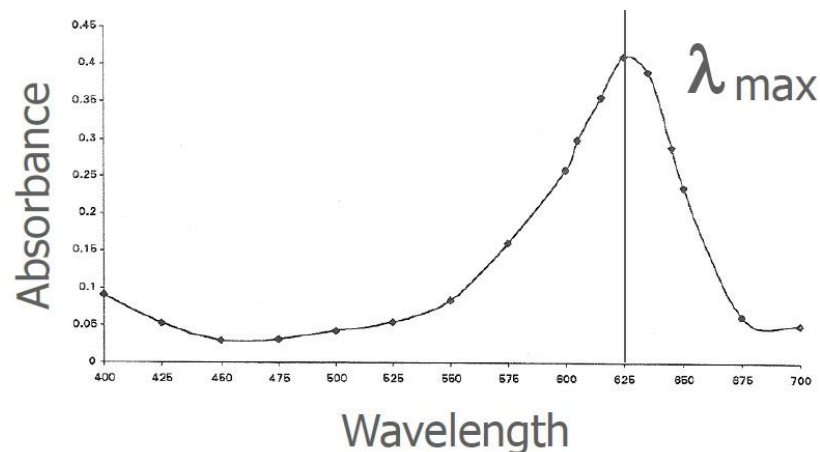


Fig. 3: The example of an absorption spectrum

All spectrometers have the following fundamental parts: a source or radiant energy, a prism or grating to isolate radiant energy to narrow wavelength regions, a device for holding the sample, and a detector for measuring light intensity. Sophisticated instruments include automatic recorders, digital readouts, computer interfaces, and arrays of detectors that allow the user to analyze a wider range of wavelengths.

The Beer-Lambert Law:



The Beer–Lambert law, also known as Beer's law, the Lambert–Beer law, or the Beer–Lambert–Bouguer law (named after August Beer, Johann Heinrich Lambert, and Pierre Bouguer) defines the mathematics relating the absorption of light to the properties of the material through which the light is traveling. The derivation of the equations used with the law involves two principle variables.

Transmissivity:

The amount of light absorbed as it is transmitted through the substance. It is defined as the ratio of the light intensity leaving the sample to the intensity entering the sample:

$$T = \frac{I}{I_0}$$

Spectrometers measure the percent (%T) transmittance of light passing through the sample.

$$\%T = \left(\frac{I}{I_0} \right) \cdot 100$$

Absorbance:

Absorbance is the amount of light absorbed expressed in logarithmic terms. It is defined as the negative logarithm (base 10) of the Transmittance.

$$A = -\log_{10} T = -\log_{10} \left(\frac{I}{I_0} \right)$$

The law states that there is a logarithmic dependence between the transmissivity of the light through the sample and the product of the “absorption coefficient (α)” of the substance and the distance (l) the light travels through the material. The absorption coefficient is a measure of the rate of decrease in the intensity of electromagnetic radiation (as light) as it passes through a given substance. The absorption coefficient can, in turn, be rewritten as a product of the molar absorptivity (ϵ) and the molar concentration (c) of the absorbing species. Molar absorptivity (also called the molar absorption coefficient or molar extinction coefficient) is a wavelength-dependent intrinsic property of the species and is a measurement of how strongly a chemical species absorbs light at a given wavelength. Incorporating these terms into the expression for absorbance results in the following:



$$A = -\log_{10} T = -\log_{10} \left(\frac{I}{I_0} \right) = \alpha \cdot l = \epsilon \cdot c \cdot l$$

Where: A is the measured absorbance (absorption units, technically unitless)

T is the amount of light absorbed passing through sample (transmittance)

I is the intensity of the radiation leaving the sample

I₀ is the intensity of the incident radiation

α is the absorption coefficient

l is the path length of the sample cell

ε Epsilon is the wavelength-dependent molar absorptivity with units of L mol⁻¹ cm⁻¹

c is the analytic concentration (Molarity) with units of mol/L

EXPERIMENTAL STUDY:

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

Many sunglasses on the market today are advertised as being able to protect your eyes from the harmful effects of ultraviolet radiation by being "blue blockers" or having ultraviolet-resistant coating. The purchase tags on most sunglasses state the percentage of ultraviolet radiation that they can block. Are these claims accurate? Are they measurable? This experiment is designed to help you find out.

The visible portion of the electromagnetic spectrum ranges from approximately 700 nm to 400 nm. This is the light we see as the familiar ROYGBIV (red, orange, yellow, green, blue indigo, and violet) colors of light. The ultraviolet portion of the electromagnetic spectrum ranges in wavelength from approximately 400 nm to 10 nm. The portion of the UV spectrum nearest the visible spectrum, from about 400 to 320 nm, is sometimes called UVA. The radiation from 320 to 290 nm is called UVB. The remaining portion of the UV spectrum is known as UVC.

The waves in the ultraviolet portion of the spectrum are relatively high in energy. You are familiar with the effects these waves have on the cells of your skin when you get a tan or a sunburn. The lower energy UVA waves are mostly responsible for the tan, while the higher energy UVB causes the sunburn.

.....700nm.....400nm.....320nm...290nm....10nm.....



←Infrared Visible UVA UVB UVC x-rays→

-----INCREASING ENERGY-----→

Your eyes can be affected by the ultraviolet radiation just as your skin can. On Earth, the atmosphere is able to screen out most wavelengths below 300 nm. Those UVA and UVB wavelengths that penetrate the atmosphere can be prevented from affecting the eyes by sunglasses that are manufactured to block this radiation.

Sunglasses are made of glass or plastic that will allow much of the visible light to be transmitted and can be designed to absorb ultraviolet radiation. Since we are interested in the amount of ultraviolet radiation that passes through the sunglasses into your eyes, we will measure transmittance of the visible and ultraviolet light through lenses. Absorbance and transmittance are terms which refer to the amounts of radiation "soaked up" or "allowed to pass through" the lenses. To conduct this experiment successfully, you should become familiar with the basics of ultraviolet spectroscopy and the difference between absorbance and transmittance of light. In this experiment you will use the PG T80+ Spectrophotometer. This instrument provides sources of both visible and ultraviolet radiation.

PROCEDURE

A. To Run % Transmittance of Standards

1. Turn on spectrophotometer from power button (at the back of the device). It will take approximately ten to fifteen minutes for the instrument to warm up.
2. Run "**UVWin Software**" from desktop and press "**OK**".
3. From left frame select "**Spectrum**".
4. From menu select "**Measure/Parameters Settings**" to enter measurement parameters.
5. From "**Measure**" tab select Absorbance (%Abs) or Transmittance (%T) mode to measure, from "**Scan Parameters**" tab adjust the starting and ending wavelength.
6. From "**Instrument**" tab select the lamps which will be used, turn off the D2 lamp if not necessary (if UV region will not be covered).
7. Press "**OK**" to save measurement settings.
8. Press "**Baseline**" to run the measurement without any sample to perform baseline correction. The screen will display 100 %T or 0 %Abs if correction is completed successfully.
9. Place the standard glass sample into the sample holder.
10. Replace the black cover and instrument chamber cover and press "**Start**".
11. When scanning has finished, press "**Yes**" to save scanning results.



B. To Run % transmittance of glasses

1. By doing Part A. Steps 1-11, the spectrophotometer should be programmed to do scans of the glasses. If you have changed any of the parameters from Part A., then repeat Steps 1-11.
2. Gently place your glasses in the spectrophotometer under the supervision of _____ the lab assistant.
3. Close the instrument chamber cover and press “**Start**”.
4. When scanning has finished, press “**Yes**” to save scanning results.

POST-LAB QUESTIONS:

1. Which kind of ultraviolet radiation contains the most energy? What is the range of wavelengths of this radiation?
2. Which form of ultraviolet radiation is most damaging to your eyes? What is the range of wavelengths for this radiation?
3. Which type of radiation should sunglasses block?
4. Describe the difference between absorbance and transmittance.
5. An absorbance spectrum shows a peak at 540 nm. What does this mean?
6. A transmittance spectrum shows a peak to 80% between 480 nm and 524 nm. What does this mean?

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7. CERAMIC PREPARATION – RHEOLOGY

Aim of the Experiment

The aim of this experiment is to explain the fundamentals of ceramic production and preparation of a ceramic slurry. Raw material preparation, grinding kinetics and rheological behaviour of the ceramic slurry will be explained in detail.

Theoretical Section

Preparation and the Rheology of a Ceramic Slurry

Drying of the droplets produces highly uniform, more or less spherical hollow granules (with a moisture content of typically 5.5 to 7%). This form of powder has high fluidity, facilitating accurate filling of the press dies and the subsequent pressing of quite large single tiles. A ceramic slurry includes the ceramic raw materials, water and auxiliary agents such as binders, deflocculants etc. In order to prepare an optimum composition, special tables are used which called as Seger Tables or Seger Rates. This Seger tables point out the ratios between the oxides which are present in the ceramic raw materials. Keeping the ratios constant is necessary while developing new compositions because every oxide has a different effect on rheology. Seger tables varies concerning the final product and the desired properties from the final product. Rheology is the science of fluidity. Fluidity can be explained by two main values which are viscosity and thixotropy. Viscosity is the value of the fluidity of a material, fluidity and viscosity has an inverse ratio between them. Thixotropy is the value of the change in viscosity with time. There are two main fluid groups which are Newtonian and Non-newtonian fluids. Newtonian fluids are just like water, their viscosity don't change with time. But for Non-newtonian fluids, viscosity changes with time. Viscosity of the Non-newtonian fluids decrease with the counting time. Ceramic slurry is a Non-newtonian fluid and it shows thixotropy property. For the rheological study of a ceramic slurry, terms like flocculation, deflocculation and deflocculant should be explained. For ceramics, if the viscosity is too low, the surface quality of the products will be low and there might be cracks on the surface. If the viscosity is too high, this will cause pinhole defects and difficulties for the transportation of the slurry (mobility). When it comes to thixotropy, it is also as important as viscosity. If the thixotropy is too high, drying time of the product will be long and if the thixotropy is too low, this will cause the product to become fragile.



Flocculation, Deflocculation, Deflocculant

When suspended in water, particles of an argillaceous material behave in two completely different mechanisms which is caused by the electrostatic charges present on the surface of the particles which can cause both attraction and repulsion. Regularly, in an acid environment, the particles are attracted to each other and this state is called as “flocculation”. In an alkiline (basic) environment, the particles repulse each other and this state is called as “deflocculation”. For the state of deloculation, the surface charges of the particles have been neutralized, this leads to the particles to remain as single separate units in suspension. Without the charges and without the attraction, there is no force holding the particles together, so this situation leads to a consequent decrease in viscosity. For the state of flocculation, the particles intend to form three-dimensional structures caused by the electrostatic attraction between them, so this situation leads to an increase in viscosity.

Deflocculants

Deflocculant term implies an additive which causes a decrease in viscosity when added. Deflocculants preclude flocculation by increasing the zeta potential between particles, which leads to the increase in repulsive forces between particles. There are several mechanisms for deflocculants to act in suspension, which can be enumerated as follows;

- Increasing the pH towards basic values by addition of bases or by hydrolysis.
- Supersession of flocculant cations which present in the double layer of clays along with alkiline cations.
- Adsorption of anions under electric field in order to achieve negative charge on particles.
- Addition of a preservative colloid.
- Elimination of flocculant ions which might be present in suspension, by precipitation or formation of coordination complexes.

Ordinarily, effects of deflocculants are submitted by a cooperation of above-mentioned mechanisms. Mechanisms does not depend on the nature of the deflocculant, it can either be organic or inorganic.

Experimental Section

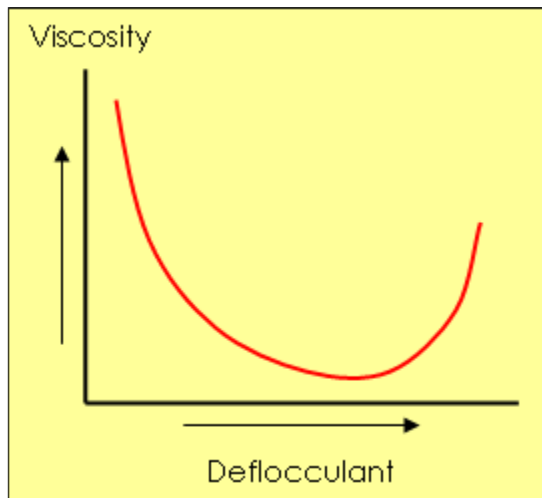
Needed Instruments

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



Application of the Experiment

First of all, raw materials are weighed and mixed regarding the composition. Then the necessary amount of water and deflocculant is added to the mix. Prepared slurry is grinded in ball mills. After the grinding process, density of the slurry is obtained by using a pyknometer. Concerning the density value of the slurry, corresponding weight is taken from the slurry and put through the 90 microns sieve. Oversize particles will give the average particle size of the grinded mix. After the determination of the average particle size, prepared slurry is mixed with a stirrer with a 700 rpm speed. During this period, in order to immobilize the viscosity level between 4 – 6 Poise (necessary value for floor tiles), deflocculant addition to the slurry is started. The amount of the added deflocculant is obtained by rule of thumb. After every addition, slurry is mixed for 3 minutes and viscosity value is determined by using an analog viscometer with a rotational speed of 20 rpm. Viscosity value of the slurry is optimized between 4 – 6 Poise without adding extra water in order to stabilize the solid concentration. To obtain the thixotrophy, slurry is put in rest for 5 minutes after every viscosity measurement. Then viscosity is measured again, difference between these two viscosity values give the thixotrophy. After the stabilization of the viscosity was achieved between 4 – 6 Poise, addition of the deflocculant is stopped. When the slurry reaches it's final viscosity, added deflocculant will not effect the viscosity until a higher amount of deflocculant is introduced into the slurry. This higher amount of deflocculant act as not as expected and it will increase the viscosity of the slurry. So the proof for the reached value of the viscosity is the stability and the following increase in viscosity with the added deflocculant.



Şekil 1. Viskozite-İlave edilen deflokülant diyagramı



Metallurgical and Materials Engineering

Laboratory-II Booklet



Results

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

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8. 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].

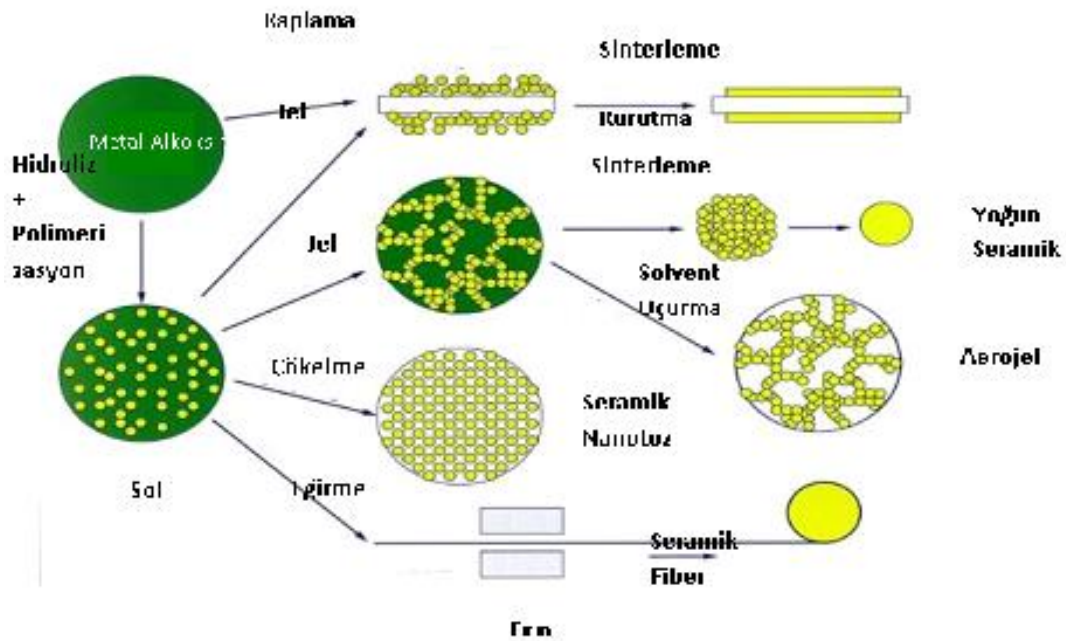


Figure 1. Sol Gel technology and products

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 (transparent) 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

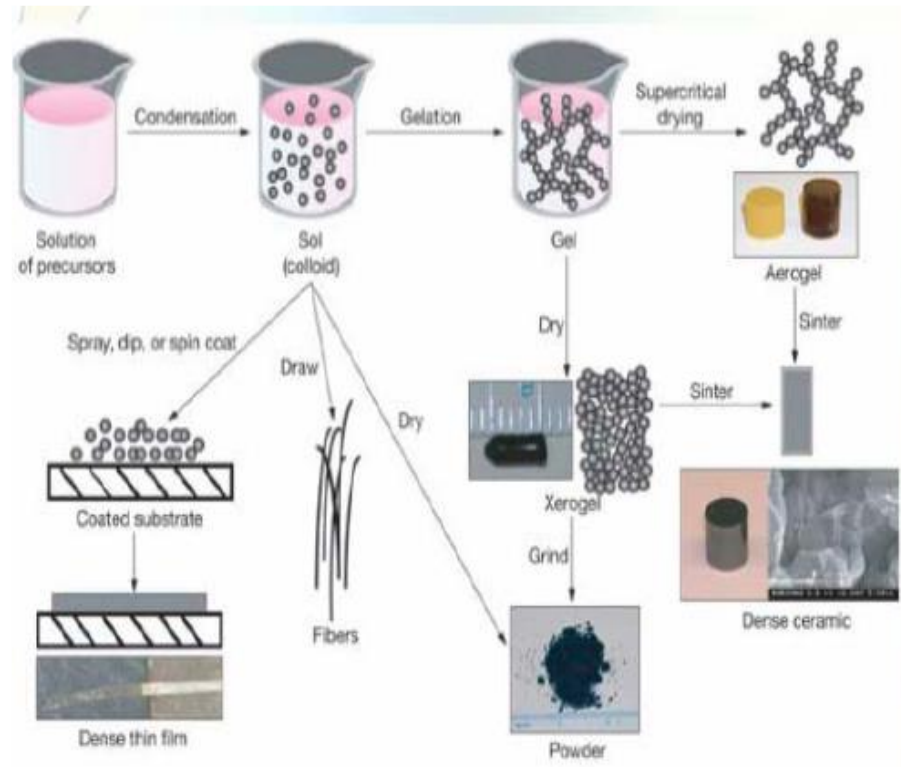


Figure 3. Sol gel steps [4].

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 OC), 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).

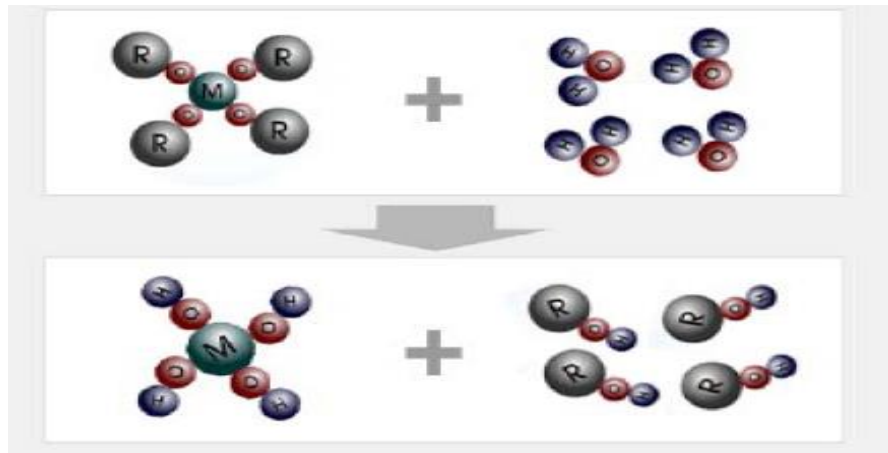


Figure 4. Alkoxide and hydrolyzed metal molecule

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.

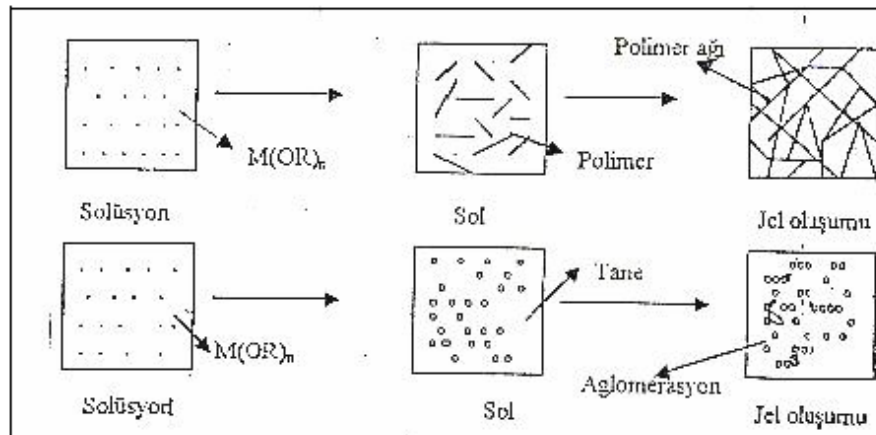


Figure 5. Polymerization Process

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 , $\text{ZrO}_2\text{-SiO}_2$, $\text{Na}_2\text{OZr-SiO}_2$).
- It allows the production of solid glass materials which cannot be obtained by cooling from liquid phase (CaO-SiO_2 , SrO-SiO_2 , $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-Al}_2\text{O}_3$).
- It allows the production of thin SiO_2 and TiO_2 ($\leq 1\mu$) 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% $\text{TiO}_2\text{-SnO}_2$)

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, $\text{Si}(\text{OC}_2\text{H}_5)_4$)
- Ammonium Fluoride (NH_4F)
- Ammonium Hydroxide (ammonia, NH_4OH)
- Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- 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 (NH₄F) and 23 mL of ammonium hydroxide (NH₄OH) 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 solid 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; SiO₂ (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 (NH₄OH) 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 SiO₂ 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 nanotop. The SiO₂ 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)

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9. BIOCERAMIC SCAFFOLD PRODUCTION

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.

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.

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].

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.

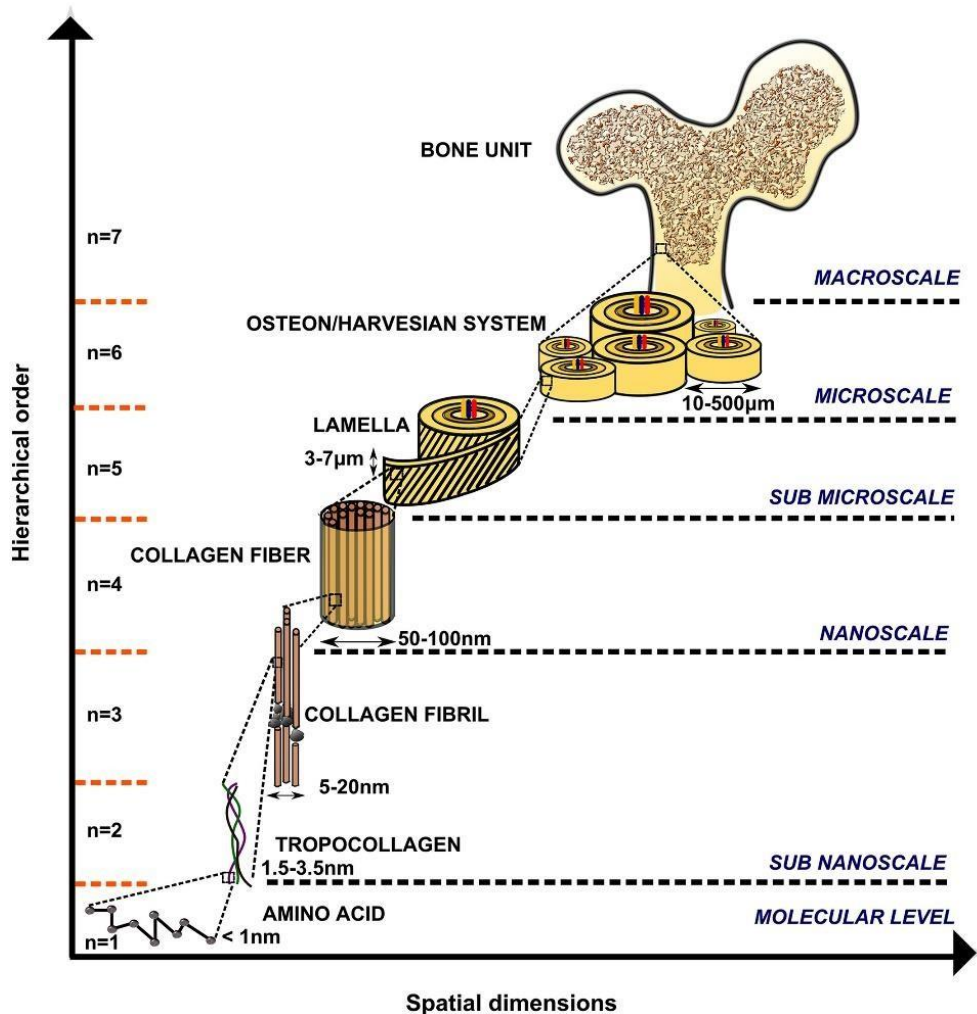


Figure 1 Hierarchical arrangement of bone in various length sizes [2]

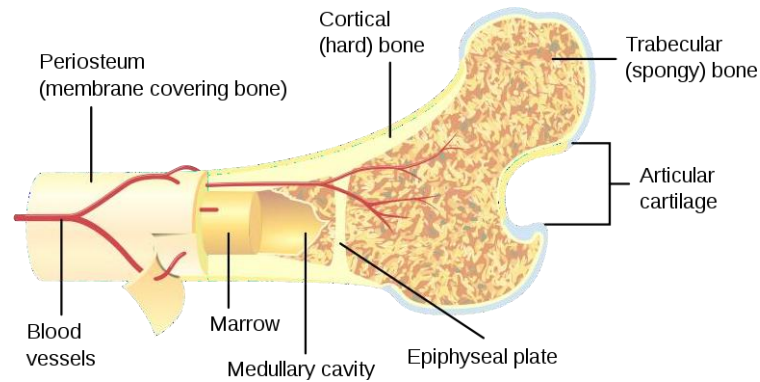


Figure 2 Cross section of bone [3]

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 phenomenon 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.

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].

SCAFFOLD PRODUCTION TECHNIQUES

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 electrospinning.

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].

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].

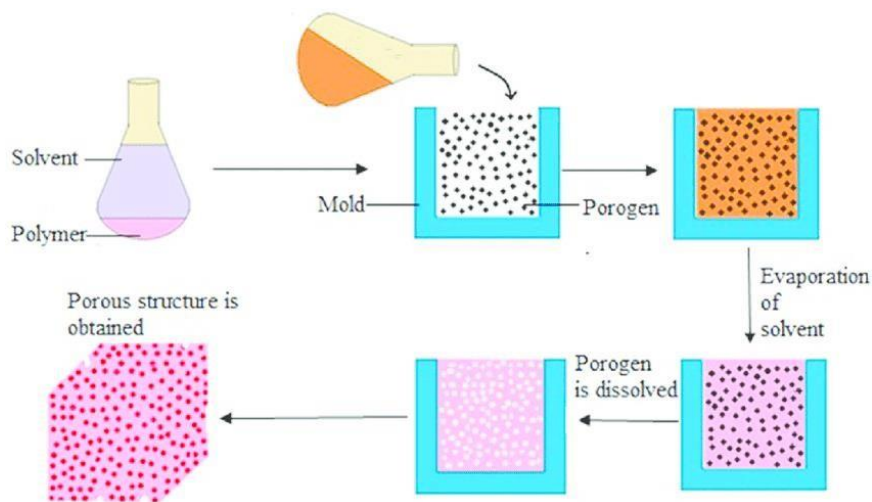


Figure 3 Schematic representation of the solvent casting /particulate leaching method [7]

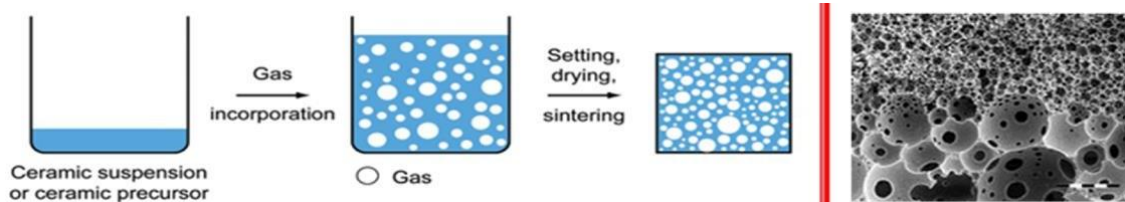


Figure 4 Schematic illustration of the gas foaming method [8]

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.

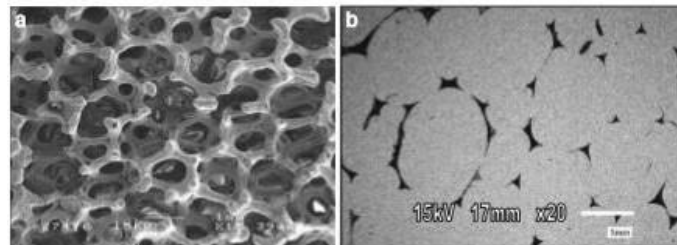


Figure 5 (a) Open porous HA structure (b) Dense HA ceramic structure with interconnected porosity [6]

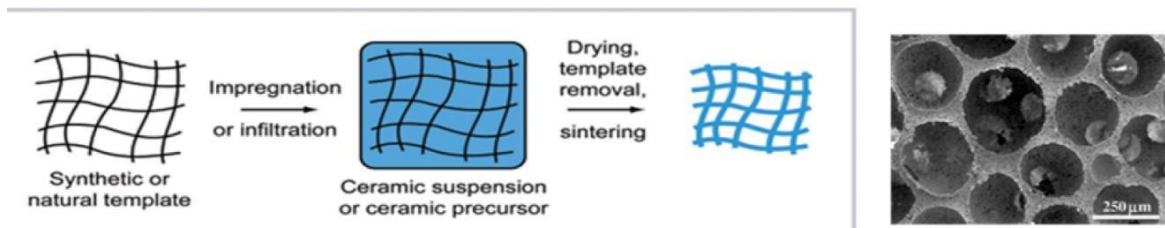
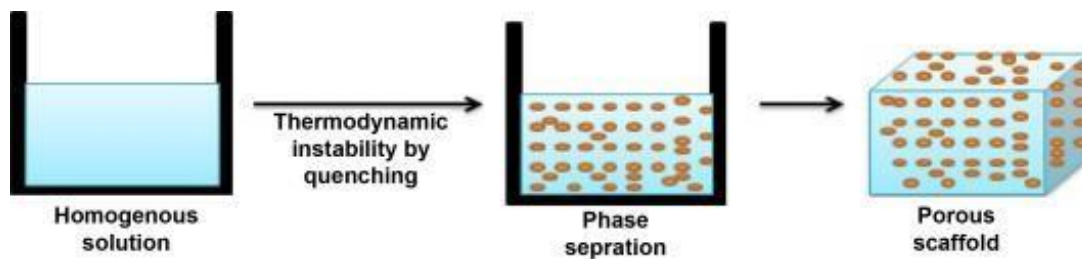


Figure 6 Schematic representation of the replica method [8]

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]

Fiber Bonding

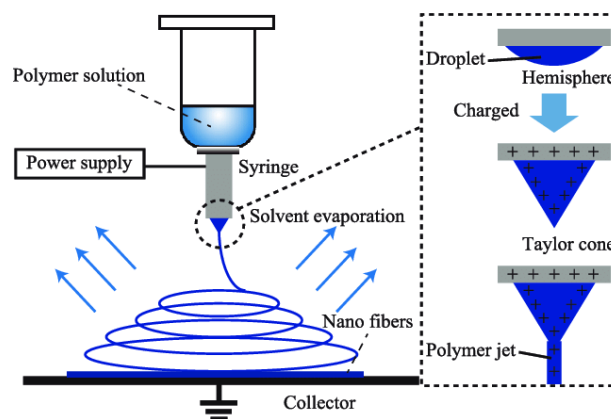
Fiber bonding method is one of the oldest tissue scaffolding production methods and developed for the purpose of using biodegradable polyglycolic acid (PGA) surgical threads as tissue scaffolds. Briefly, a solution of poly-L-lactic acid (PLLA)

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].

Electrospinning

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]



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].

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].

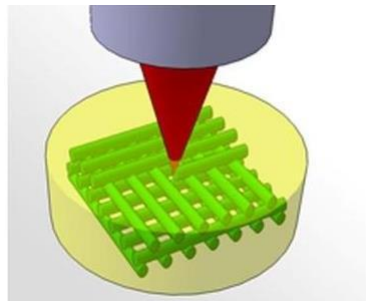


Figure 9 Schematic representation of scaffold production with FDM [11]

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 Stirrer, pH Meter, Analytical Balance, Oven, Sintering Furnace
- Chemicals: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, HCl, NH_4OH , Porogen (Starch), Binder (Triethyl phosphate), Distilled water

METHODS

SYNTHESIS OF HYDROXYAPATITE CERAMICS

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



- 1M calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] and 1.2M diammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$] 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 mL/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 finally ground in agat mortar.

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.



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.

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.

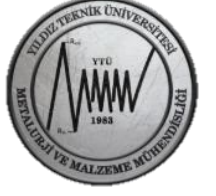
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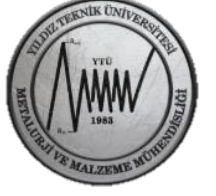


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