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SOL-GEL PROCESS.

Sol-gel process is a widely adopted low temperature process for the preparation of porous as well as some bulk materials of both amorphous and crystalline nature, The major steps involved are,

(i) The preparation of the sol involving dispersion of the solid or hydrolysis of a precursor.

(ii) Ageing of the sol to form a gel.

(iii) Heat treatment.

→ In the first step, a sol (colloidal suspension of 1-100nm sized particles) is prepared by dispersing insoluble solid such as oxide or hydroxide in water at controlled pH, so that the solid particles remain suspension without precipitating out. Alternatively, the sol may be prepared by the addition of a precursor which reacts with the solvents to form a colloidal products.

For e.g., the precursor, usually, a metal alkoxide is dissolved in water to yield a sol of metal oxide as the alkoxides undergoes hydrolysis.

$$M(OR)_n + x \cdot nH_2O \longrightarrow M(OH)_x(OR)_{n-x} + xROH \quad \text{—(1)}$$

; where M is metal ion and R is alkyl group.

→ In the second step, i.e. polymerisation step, the sol is allowed to stand to form a thick gel by ageing or may be heated. The gel is a semi rigid solid consisting of the solvent in a framework of solid particles, which is either colloidal (potentially a concentrated sol) or polymeric in nature. The gel can be shaped into fibers or other required forms by appropriate treatment. (Fig.-1)

→ In the final step, the gel is given a heat treatment to remove the solvent or decompose anions such as alkoxides or carbonates to give oxides. The heat treatment also facilitates the rearrangement of the ~~structure~~ structure of the solid and crystallization.

→ The heat treatment ~~also facilitates to~~ may be simple drying to form porous ceramic materials or calcining and sintering (heating to temperatures below the boiling of the solid product and simultaneously applying pressure) to produce compact solids.

→ For e.g. Lithium niobate, a ferroelectric material used in optical switches, is prepared by mixing the alcoholic solution of lithium ethoxide (LiOEt) and niobium ethoxide $[Nb_2(OEt)_{10}]$ followed by addition of water to yield the sol of hydroxy ethoxides by partial hydrolysis of the ~~ee~~ ethoxides. The sol condenses to form the polymeric gel with metal oxygen links which on ~~heat~~ heat treatment yield the product lithium niobate.

→ After drying, ~~step~~ a step is carried out between 670 K and 1070 K to drive off the organic residues and chemically bound water. Dehydration and dealcoholation are polycondensation reactions that are occurred during this step, and may be represented as follows,

$$\left.\begin{array}{l} -M-OH + OH-M- \rightarrow M-O-M + H_2O \text{ (Dehydration)} \\ -MOH + RO-M- \rightarrow MO-M + ROH \text{ (Dealcoholation)} \end{array}\right\} - (2)$$

The various steps involved in the solgel process is schematically represented in Fig. 1

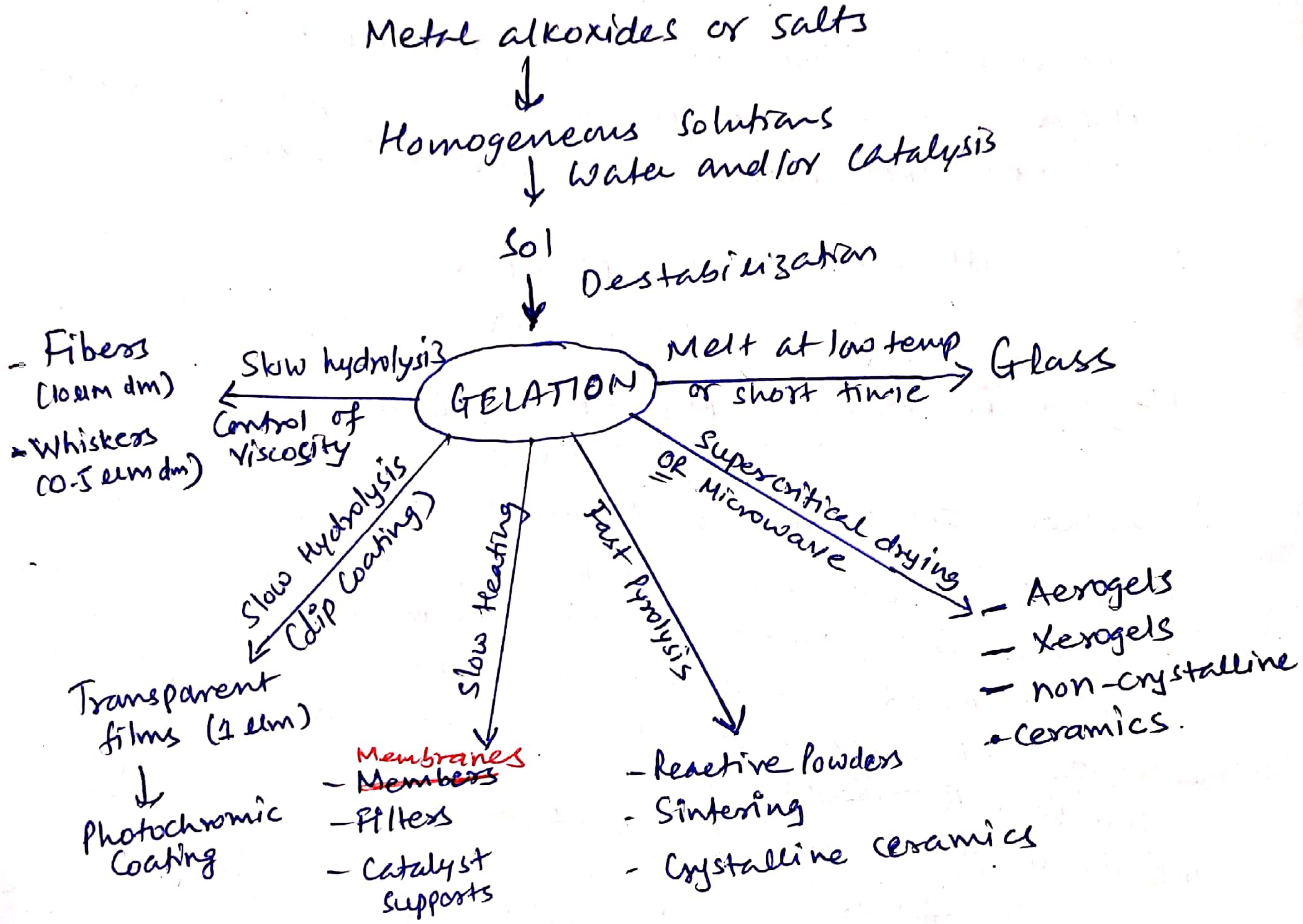

Fig. 1. Sol-gel Process

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$$-M-OH + OH-M- \rightarrow M-O-M + H_2O$$
(Dehydration) —— (23)

$$-M-OH + RO-M \rightarrow -M-O-M + ROH$$
(Dealcoholation).

<u>Advantage</u>: The solgel method has the advantage of preparing amorphous materials such as glass and crystalline solution at low temperatures.
In the preparation of glass, the mixture of raw materials consisting of metal silicates, phosphates and borates is bought into solution and hydrolysed at controlled pH to yield the gel ~~cell~~ which is then dehydrated to form the glass.
- In the preparation of porous high surface area crystalline solids such as silica gel, the precursor isopropoxide is ~~hydroze~~ hydrolyzed at controlled pH and dried to dehydrate the gel.

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Sol-gel Chemistry:

Sol-gel chemistry has evolved as a powerful approach for preparing inorganic materials such as glasses and ceramics. The name, "sol-gel" is given to the process, because of the distinctive viscosity increase that occurs at a particular point in the sequence of steps. A sudden increase in viscosity is the common feature in sol-gel processing, indicating the onset of gel formation.

⇒ The terms commonly employed in sol-gel processing are -

(i) Precursors: They are starting materials, in which the essential basic entities are present in the correct stoichiometry for network formation in subsequent treatment stages. Precursors generally used in sol-gel process are; alkoxides, inorganic salts (chlorides, nitrates etc), organic salts (acetates, acetylacetonates etc.)

(ii) Sol: A sol is a dispersion of colloid particles in a liquid, that is typically small enough (1-100 nm) to remain ~~suspended~~ suspended in the liquid.

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(iii) <u>Colloids</u> : They are nano-scaled entities, dispersed in a fluid.

(iv) <u>Gels</u> : A gel consists of atleast two phases, a solid network that entraps a liquid phase. The gel is the colloidal dispersed substance which forms a continuous ramifying coherent network that is interpenetrated by a system, usually the liquid.

→ They are viscoelastic bodies that have interconnected pores of submicrometric dimensions. Gels are usually classified according to the dispersion medium used, e.g. hydrogel or aquagel, alcogel and aerogel for water, alcohol and air respectively. The ~~sol gel~~ sol gel process is the transformation of a system of colloidal particles in a solution into a disordered, branched continuous network, which is interpenetrated by a liquid.

(v) Xerogel: The term xerogel is used to designate "dry gels". They are obtained when the liquid within the gel is removed by simple evaporation.

(vi) Aerogel: When the pore liquid is removed as a gas phase from the interconnected solid gel network about its critical temperature and pressure (under supercritical conditions) the solid network does not collapse, and a low density aerogel is produced. The drying step is performed inside an autoclave which allows to overpass the critical point (P_c, T_c) of the solvent.

(vii) Cryogel: A "cryogel" results from a freeze-drying process. They are produced from gels in which the liquid phase is first frozen into a solid and then sublimed. The vapour is removed by vacuum pumping.

In general, sol-gel technique can be regarded as ~~a~~ the preparation of ~~a~~ sol, gelation of the sol and removal. The overall sol-gel process can be represented by the following sequence of transformation

Precursor ⟶ Sol ⟶ Gel ⟶ Product

In a ~~typ~~ typical case, the sol-gel process involves hydrolysis of the salt under suitable conditions to form the corresponding hydroxide (sol) and polycondensation to form a thick gelatineous ~~hydroxide~~ ~~oxid~~ hydrous ~~ox~~ oxide (the gel)

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- Thermal stability: It is directly related to creep behaviour. Thermal stability is the ability of a material to maintain its mechanical properties at varying temperatures.
- Materials operating at low temperatures have a tendency to fast fracture as they lose their ductility, whereas materials operating at high temperatures lose their electromechanical properties and experience changes in strength of materials.

- The increased presence of dislocation and grainboundaries prevents movement of dislocations, thus preventing plastic deformation (due to increasing in tensile strength)

- Corrosion is a surface phenomenon in which a metal forms an oxidation layer which alters its mechanical properties. Corrosion occurs when there is surface defects. ~~Grain~~ Grain boundaries interact with the surface layer of the material, causing decrease in corrosion of material.

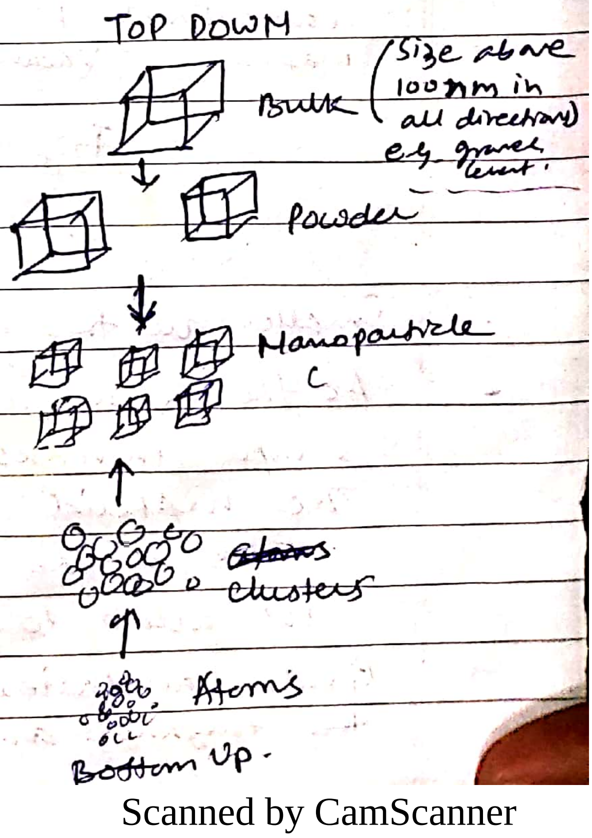
Thus, the strength of the material increases when grain size is reduced.

#. PRODUCTION METHODS:

Metals having grain sizes smaller than 1 µm (1000 nm) may be produced in two fundamentally different ways:

Bottom up approach refers to the build up of a material from the bottom atom by atom, molecule by molecule or cluster by cluster (viz Deposition techniques and Nanoscale building blocks)

- Top down approach refers to slicing or successive cutting of a bulk material to get nanosized particle



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Significance of Grain size:

Source: Nicola Ergo (Slideshare)
(the importance of grainsize

(I) Grain size: It is a microstructural parameter in dictating the properties of a polycrystalline materials.

(II) Ultrafine Grain materials (UFG): They have one dimension in the order of 100-1000 nm. UFG material further deformed to produce nanomaterials.

(III) Nanocrystalline grain boundaries store interstitial defects, then fire them back into the matrix to annihilate passing vacancies, destroying both defects and healing the material. Whereas in conventional materials, interstitials diffuse to the surface, leaving internal voids and causing the swell.

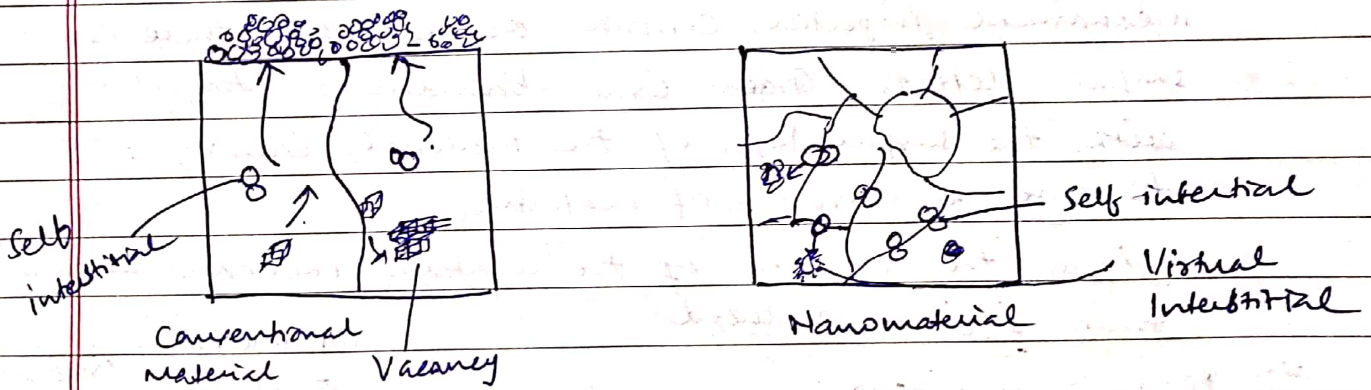

Fig. Difference in Grain size between Conventional and Nanomaterials

- Smaller are the grains more are the grain boundries
- As the grain size decreases, the homogeneity of the sample increases. High purity is associated with homogeneity. The material has the same properties Throughout the sample as the grain size are significantly small and do not allow to many impurities and irregularities.
- Grain boundaries resist ~~the~~ cracks growth, thus increasing fracture ~~too~~ toughness. and it is directly related to durability (deformation under stress/cyclic loading)