

# **MME 3307**

# **Glass ceramics**

Part 2

# Glass-Ceramics

- Polycrystalline material produced through controlled crystallization (devitrification) of glass.
- Amorphous phase & one or more crystalline phases
- Share many properties with both glasses and ceramic
- 30% to 90% crystallinity and yield an array of materials with interesting properties like
  - zero porosity, high strength, toughness, low/even negative thermal expansion, high temperature stability.

- The properties can be varied by changing the composition of the base glass or/and through the crystallization process.
- A wide variety of glass-ceramic systems exists, e.g.,
  - $\text{Li}_2\text{O} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$ -System (LAS-System),
  - $\text{MgO} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$ -System (MAS-System),
  - $\text{ZnO} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$ -System (ZAS-System).

- Glass-ceramics are mostly produced in two steps:
  - First, a glass is formed by a glass manufacturing process. The glass is cooled down and is then reheated in a second step.
- In this heat treatment the glass partly crystallizes. In most cases nucleation agents are added to the base composition of the glass-ceramic. These nucleation agents aid and control the crystallization process. Because there is usually no pressing and sintering, glass-ceramics have, unlike sintered ceramics, no pores.

# Crystallization Process

- The crystallization, or devitrification, of glass to form a glass-ceramic is a heterogeneous transformation and as such consists of two stages
  1. nucleation stage
  2. growth stage.

## Growth stage.

- Once a stable nucleus has been formed the crystal growth stage commences. Growth involves the movement of atoms/molecules from the glass, across the glass-crystal interface, and into the crystal.

## Nucleation stage

- In the nucleation stage small, stable volumes of the product (crystalline) phase are formed, usually at preferred sites in the parent glass.

# Processing Routes for Glass-Ceramic Production

- Conventional Method (Two-Stage)
- Modified Conventional Method (Single-Stage)
- Petrurgic Method
- Powder Methods
- Sol-Gel Precursor Glass

# Biomedical applications



The glass ceramic is a material that is molded to the desired shape as a crystal, then subjected to a heat treatment to induce a devitrification.





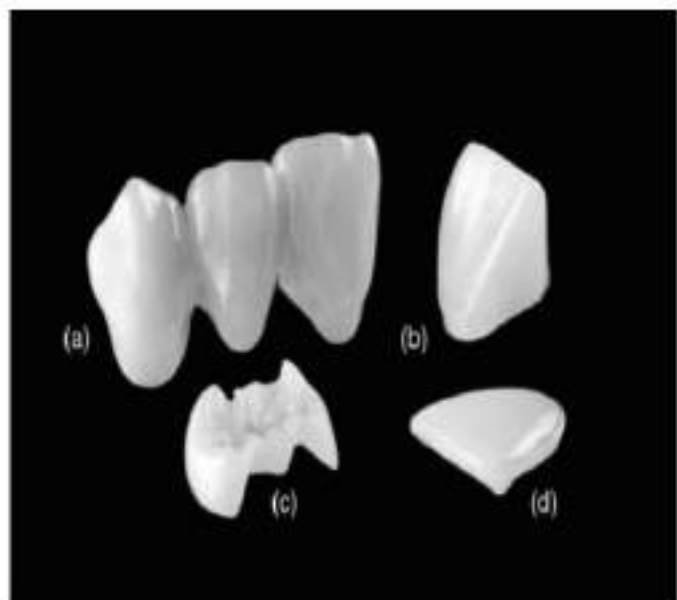



Figure 4.43 Glass-ceramic metal-free restorations: (a) Dental bridge (with two types of glass-ceramics: lithium disilicate and fluoroapatite) of IPS e.max<sup>®</sup>-type and leucite glass-ceramics as (b) crown, (c) inlay, and (d) veneer (from left to right and from the bottom to the top of the figure) of IPS Empress<sup>®</sup>-type (products of Ivoclar Vivadent AG). See color insert.



Figure 4.47 IPS Empress<sup>®</sup> glass-ceramic. (a) Preoperative situation showing four amalgam fillings, (b) four glass-ceramic inlays/onlays of IPS Empress<sup>®</sup> staining technique (courtesy of: dentist: Brodbeck; dental technician: Sisera, Arteco Dentaltechnik, Zürich, CH). See color insert.



Fig. 2 Glass-ceramic teeth.

**Desempenho digital insuperável numa câmara SLR**

Profissional, coroando doze anos de atuação no mercado de câmeras digitais, a DCS Pro 14n difere de todas as anteriores por sua eletrônica no desenho do corpo e no sensor de imagens CMOS. Bonita, leve e ágil, com recursos SLR para aplicações profissionais, revela toda sua extensibilidade. Construída sob encomenda e com exclusividade para a Kodak Profissional em F NIKON, tornando-se compatível com toda a linha atual de objetivas e acessórios.

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Disponível com o primeiro sensor CMOS **O novo Software Kodak DCS PI**  
 disponível do filme 35mm (24 x 36 mm)

Fig. 4. From left to right: parent glass, glass-ceramic with 97 percent crystallinity and glass-ceramic with 50 percent crystallinity. Grain size is about 20 micrometers.

# Coatings

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## Half Mirror Coating

Half mirror coating allows the flames to appear in the forefront of the glass, while the background of the stove remains visually obscured. When the flames are extinguished, the stove interior fades into the background so that the decorative exterior of the hearth remains the visual focus. The darker the fireplace interior, the more dramatic the effect.

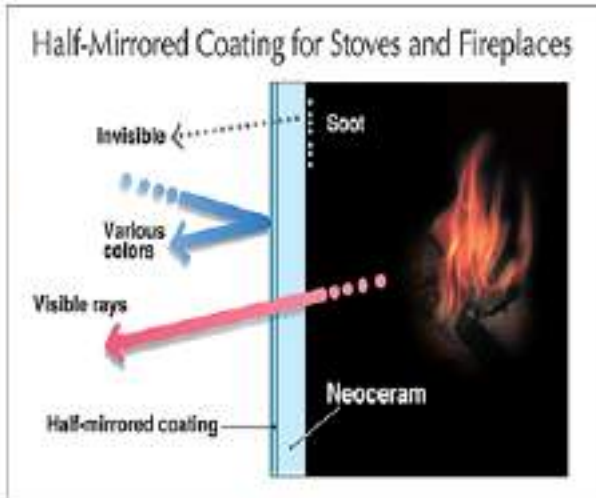






Figure 4.4 Examples of the uses of MACOR® glass-ceramics.

- Aerospace industry  
More than 200 special parts of the U.S. space shuttle orbiter are made of this glass-ceramic. These parts include rings at all hinge points, windows, and doors.
- Medical equipment  
The accurate machinability of the material as well as its inert character are particularly important in the production of specialized medical equipment.
- Vacuum technology  
MACOR® glass-ceramics make excellent insulators. They are widely used to manufacture equipment for vacuum technology. Compared with sintered ceramics, glass-ceramics are pore free.
- Welding  
MACOR® is used in welding equipment, as the material exhibits excellent nonwetting properties with regard to oxyacetylene.
- Nuclear-related experiments  
MACOR® is not dimensionally affected by irradiation. As a result, applications in this field are possible.

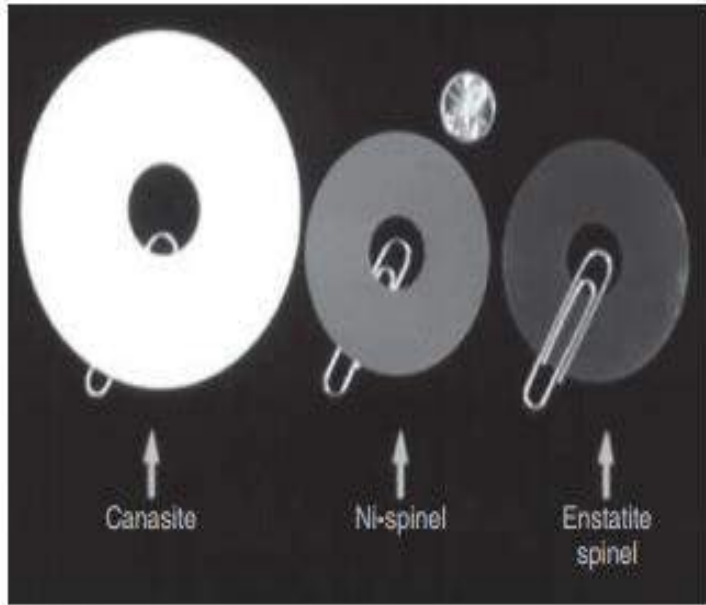


Figure 4.5 Spinel-enstatite glass-ceramic as a magnetic memory disk substrate, in comparison with a canasite disk and a nickel-spinel glass-ceramic.

- Glass ceramics spinel-enstatite material provide smoother surface roughness.
- The distance of the probe is on 20 nm.
- 100 – 165 Gpa for Young Modulus, to prevent flutter during high rotational speed up to 10k rpm.



Figure 4.7 Pyroceram Corning Ware® 9608 dishes

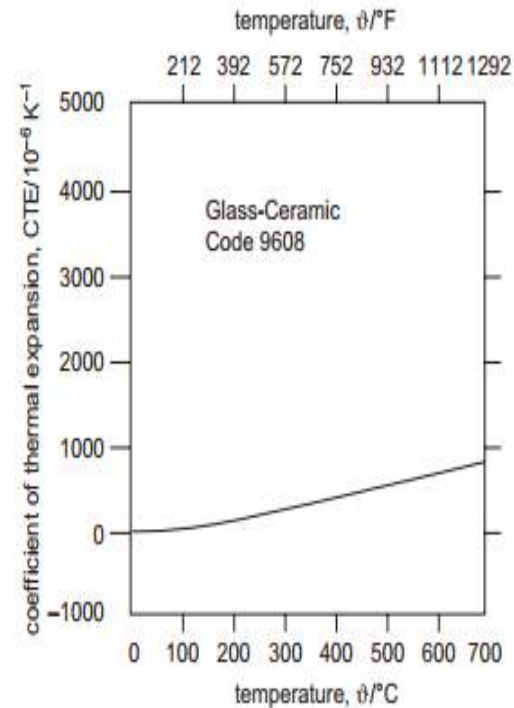


Figure of Co

#### 4.2.1 $\beta$ -Spodumene Solid-Solution Glass-Ceramic

Stookey (1959) developed one of the first glass-ceramic materials marketed worldwide for use as household crockery. The glass-ceramic in question was called Pyroceram® 9608 (it is also known as Corning Ware® 9608). The material contains the main crystal phase  $\beta$ -spodumene solid solution, with minor rutile. This particular glass-ceramic is white and exhibits a low CTE of  $0.7 \cdot 10^{-6}/\text{K}$  (Fig. 4.6). The economical manufacturing techniques of Pyroceram 9608 in the Corning Glass Works, USA, allowed the material to be used for low-cost kitchen applications and thermal-shock-resistant cooking dishes that could withstand high temperature fluctuations.



Figure 4.9 Vision® glass-ceramic in the form of domestic products.

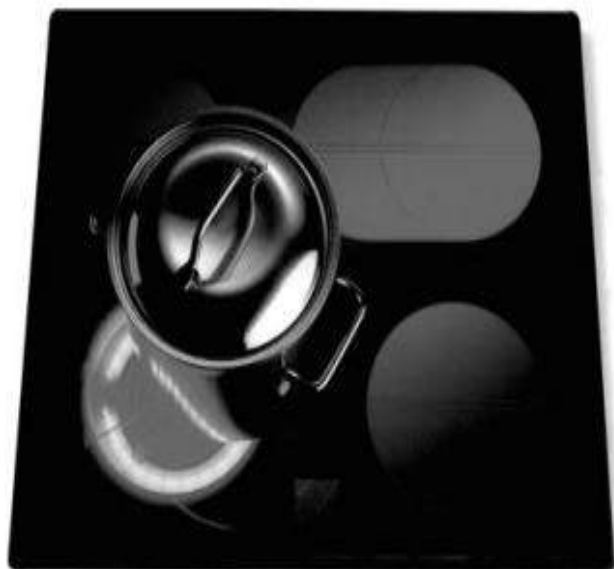


Figure 4.10 EuroKera® cooktop panels.



Figure 4.13 Processing of 8.2 m Zerodur® glass-ceramic telescope mirror.



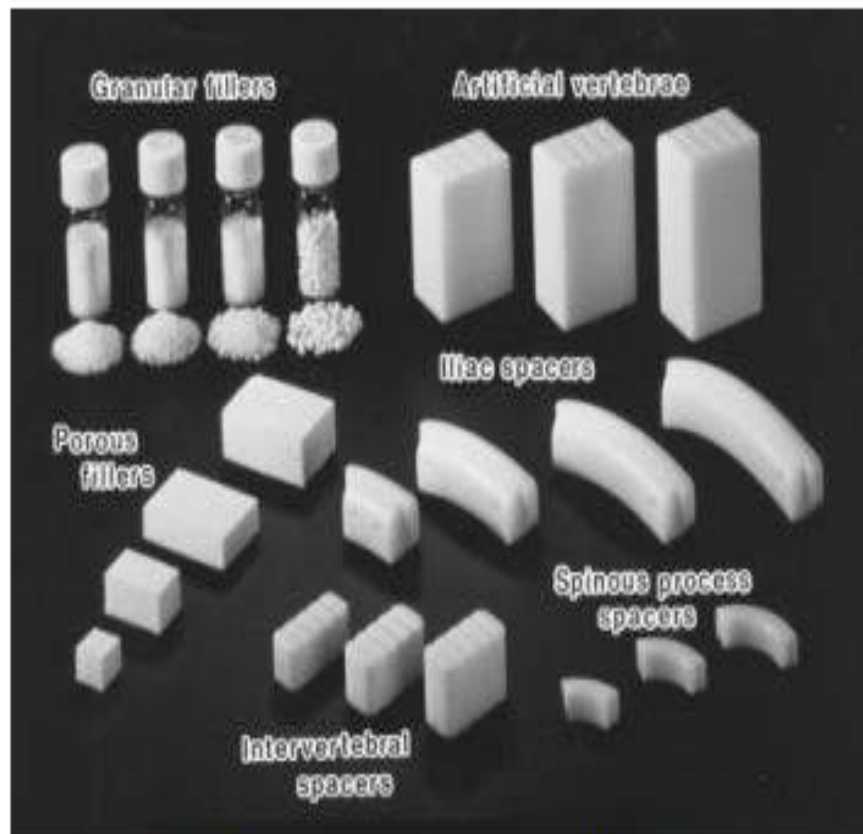


Figure 4.41 Artificial vertebrae, spacers, and fillers of CERABONE A-W

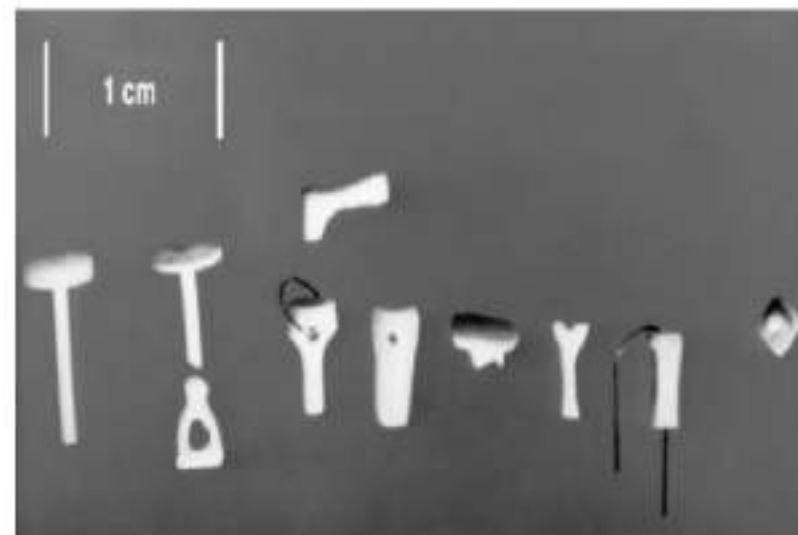


Figure 4.42 Middle-ear implants of BIOVERIT® II.



Figure 4.53 Glass-ceramics machining with CAD/CAM technology: Blue block of IPS e.max® CAD (precursor product as lithium metasilicate glass-ceramic) and leucite glass-ceramics of IPS Empress® CAD (machined product and block). Materials from left to right. See color insert.





Figure 4.68 Fire-resistant glass-ceramic Firelite®.



Figure 4.67 Neopariés™ glass-ceramic as a building material.

**MME 3307**  
**Metal/ Metallic Glass**

Part 3

# INTRODUCTION

- The material which has the properties of both metals and glasses is known as metallic glass or metglass.
- They have high strength, good magnetic properties and better corrosion resistance.
- METALLIC GLASS = AMORPHOUS METAL



1. **Crystalline** : We can see that crystal atoms have equal gap from each other thus forms a strong bond of contact.
2. **Polycrystalline** : Polycrystalline atoms have less contact or bonding than the crystalline atoms.
3. **Amorphous** : These structure forms the metallic glass.



# GLASS TRANSITION TEMPERATURE( $T_g$ )

- **Metallic glass is prepared by cooling a metallic liquid having disordered structure.**  
[ RATE OF COOLING IS  $2 \times 10^6 \text{ }^\circ\text{C}$  ]
- **The temperature at which the transition from liquid to solid is known as glass transition temperature.**

$$T_g = 20^\circ \text{ C TO } 300^\circ \text{ C}$$

# PREPARATION OF METALLIC

## GLASS:

### Principle:

“Extreme rapid cooling of molten metal alloy called ‘*quenching*’ “.

Cooling so rapidly that there is no formation of crystalline structure forming solid frozen in liquid structure.

There are three types of preparation

- \*Melt Spinning system
- \*Twin Roller system
- \*Melt Extraction system



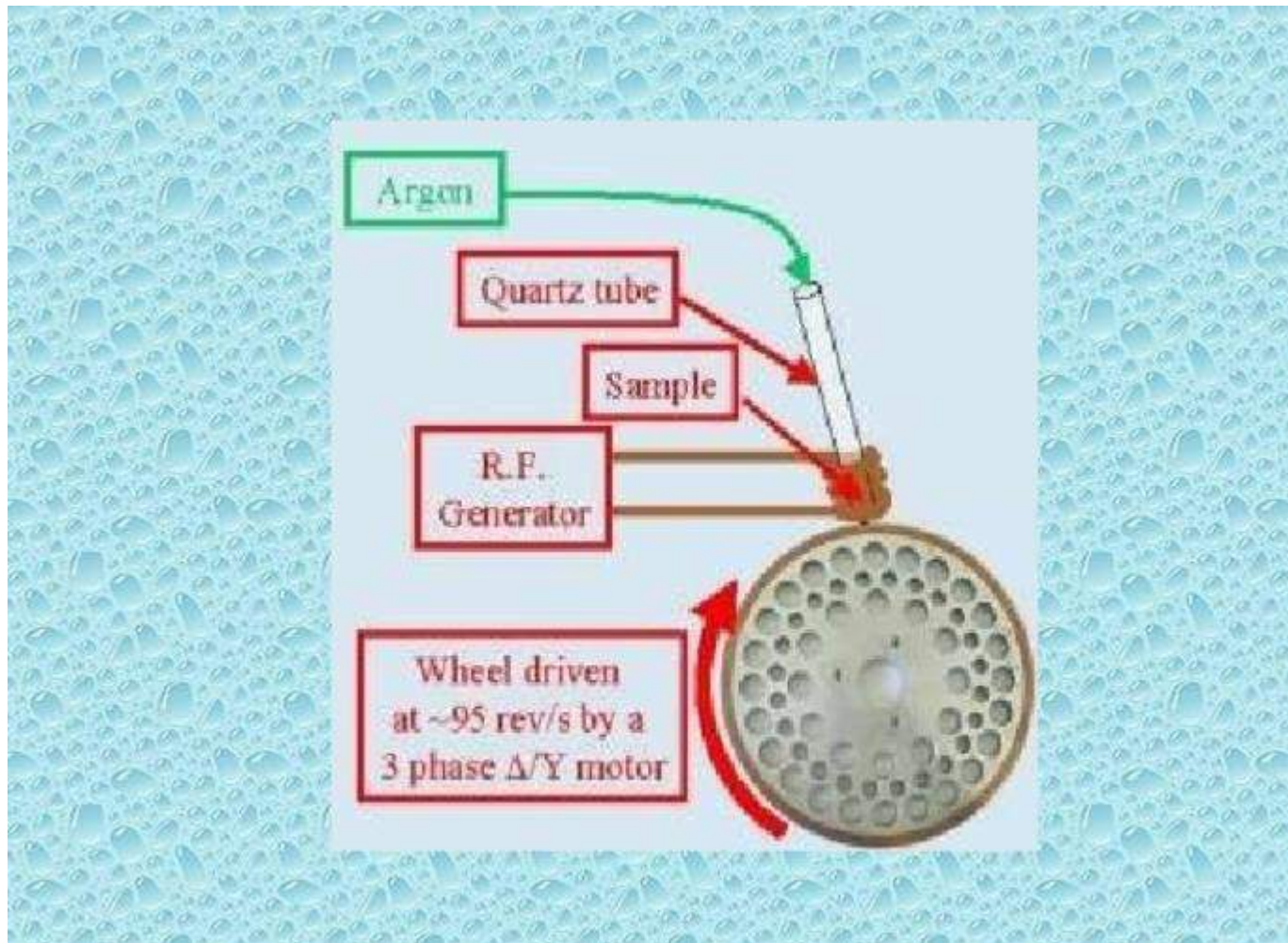
## **PREPERATION MELT SPINNING**

- **Melt spinner contains refractory tube , copper disc, induction heater.**
- **Mixture of alloy has taken in refractory tube and is heated to very high temperature by using induction furnace.**
- **The molten alloy is ejected through fine nozzle at the bottom of refractory tube.**

## **PREPERATION MELT SPINNING**

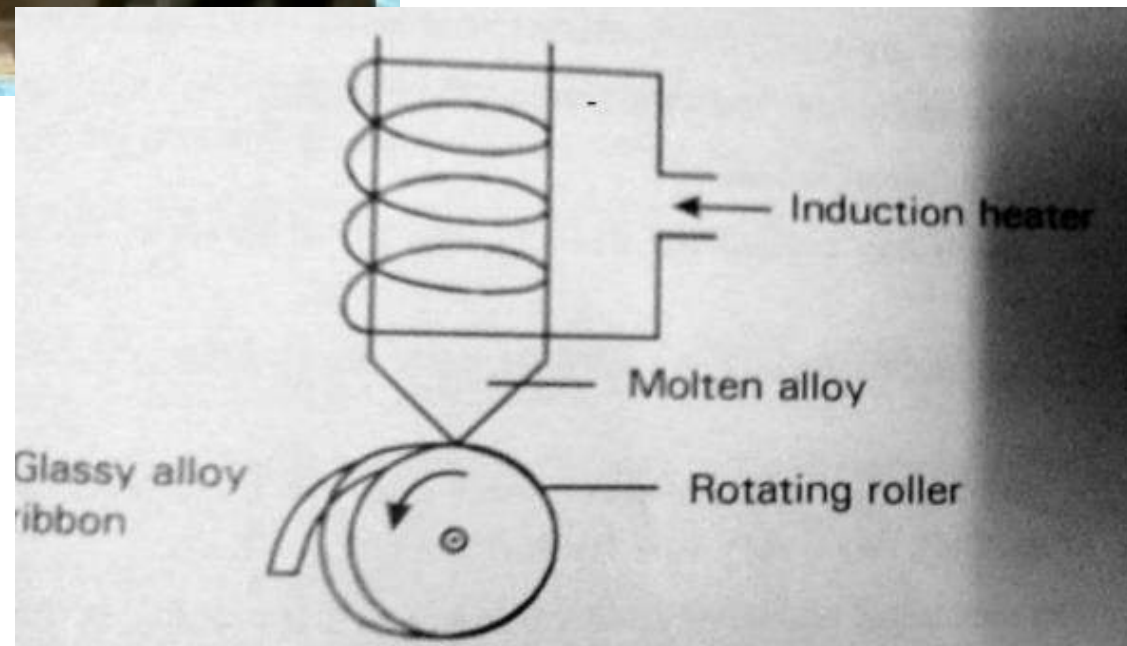
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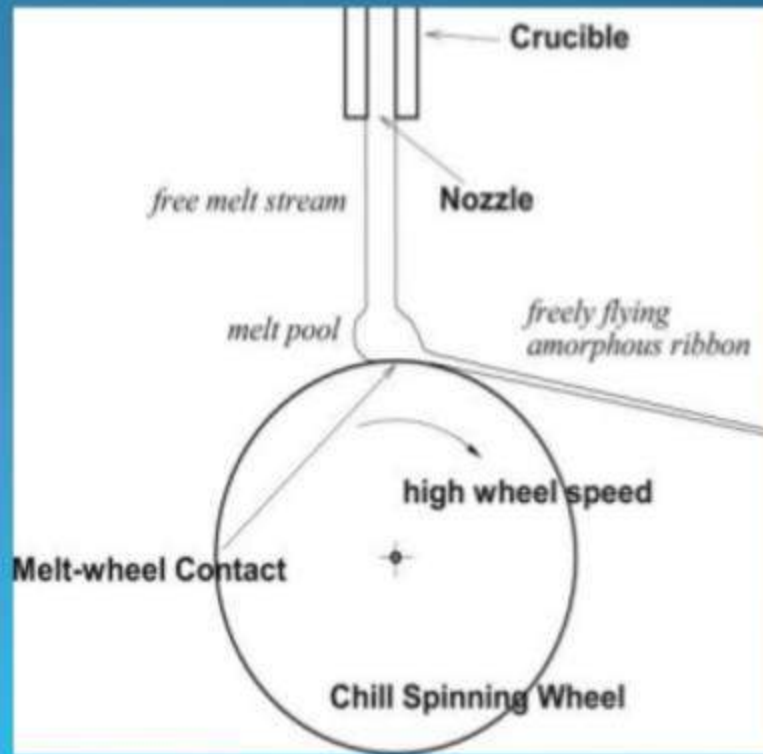
- Molten alloy is suddenly cooled while that is interact with the wheel and that is solidified.

# MELT SPINNING



<https://www.youtube.com/watch?v=L00HbH8Vla8>

# MELT SPINNING SYSTEM:

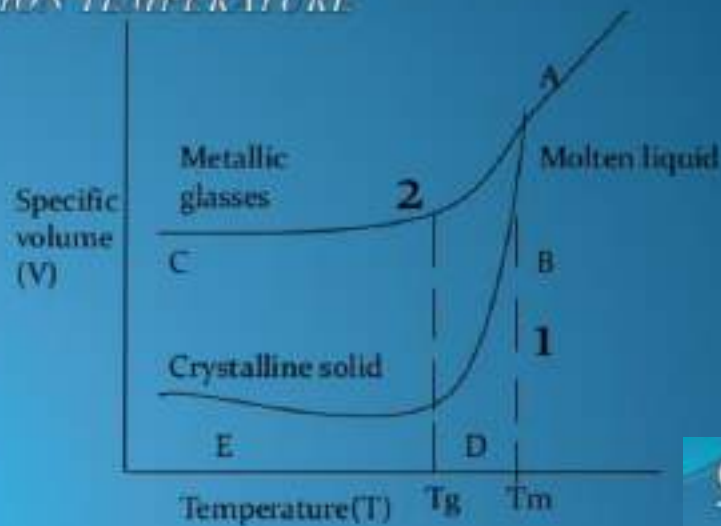




# GLASS TRANSITION

## TEMPERATURE:

THE TEMPERATURE AT WHICH TRANSITION FROM LIQUID TO SOLID OCCURS IS KNOWN AS GLASS TRANSITION TEMPERATURE.



### Case(1):

The curve ABDE shows the change from molten liquid to crystalline solid by normal cooling at a temperature called MELTING POINT TEMPERATURE.

### Case(2):

The curve ABC shows the change from molten liquid to metallic glass by rapid cooling at GLASS TRANSITION TEMPERATURE.

The glass transition temperature of metallic glasses is 20-30°C.

# CLASSIFICATION

- **METAL-METALLOID GLASS**  
(Fe,Co, Ni ) and(B , Si, S, P )
- **METAL – METAL GLASS**  
Nickel - Niobium(Ni-Nb)  
Magnesium-Zinc (Mg-Zn)  
Copper-Zirconium (Cu- Zr)  
Hafnium-Vanadium(Hf-V)

## METAL-METAL METALLIC GLASS:

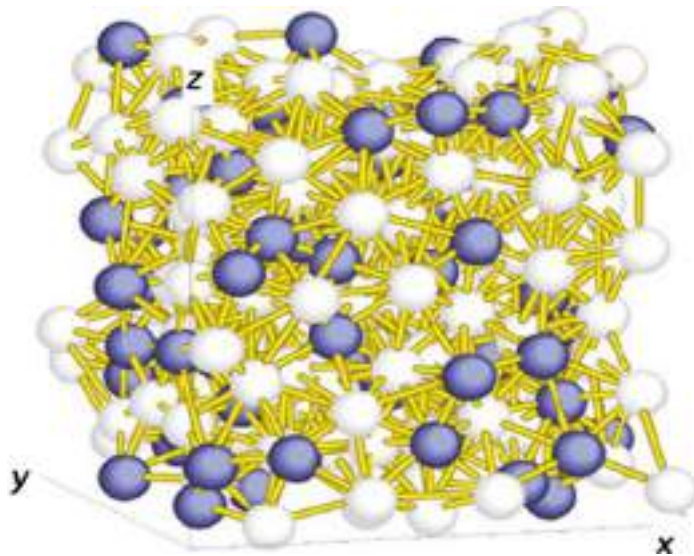
Combination of metals

METAL	METAL
Nickel(Ni)	Niobium(Nb)
Magnesium(Mg)	Zinc(Zn)
Copper(Cu)	Zirconium(Zr)

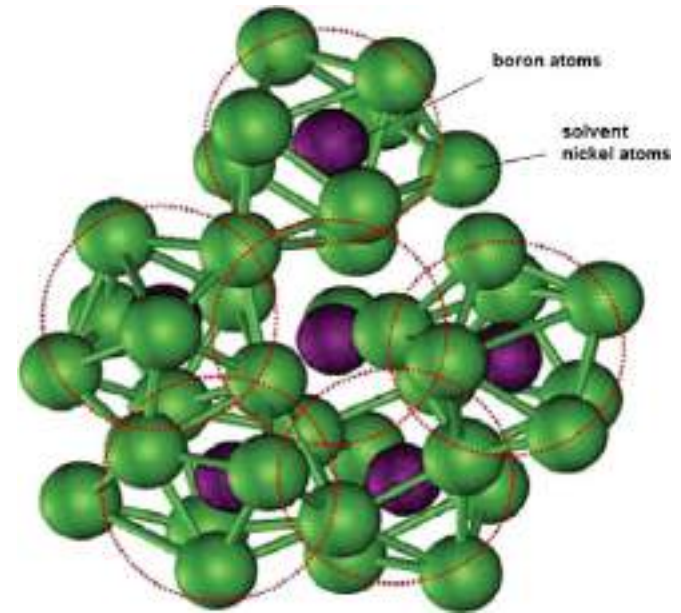
## METAL- METALLOIDMETALLIC GLASS:

Combination of metal and metalloids

METAL	METALLOIDS
Fe,Co,Ni	B,Si,C,P

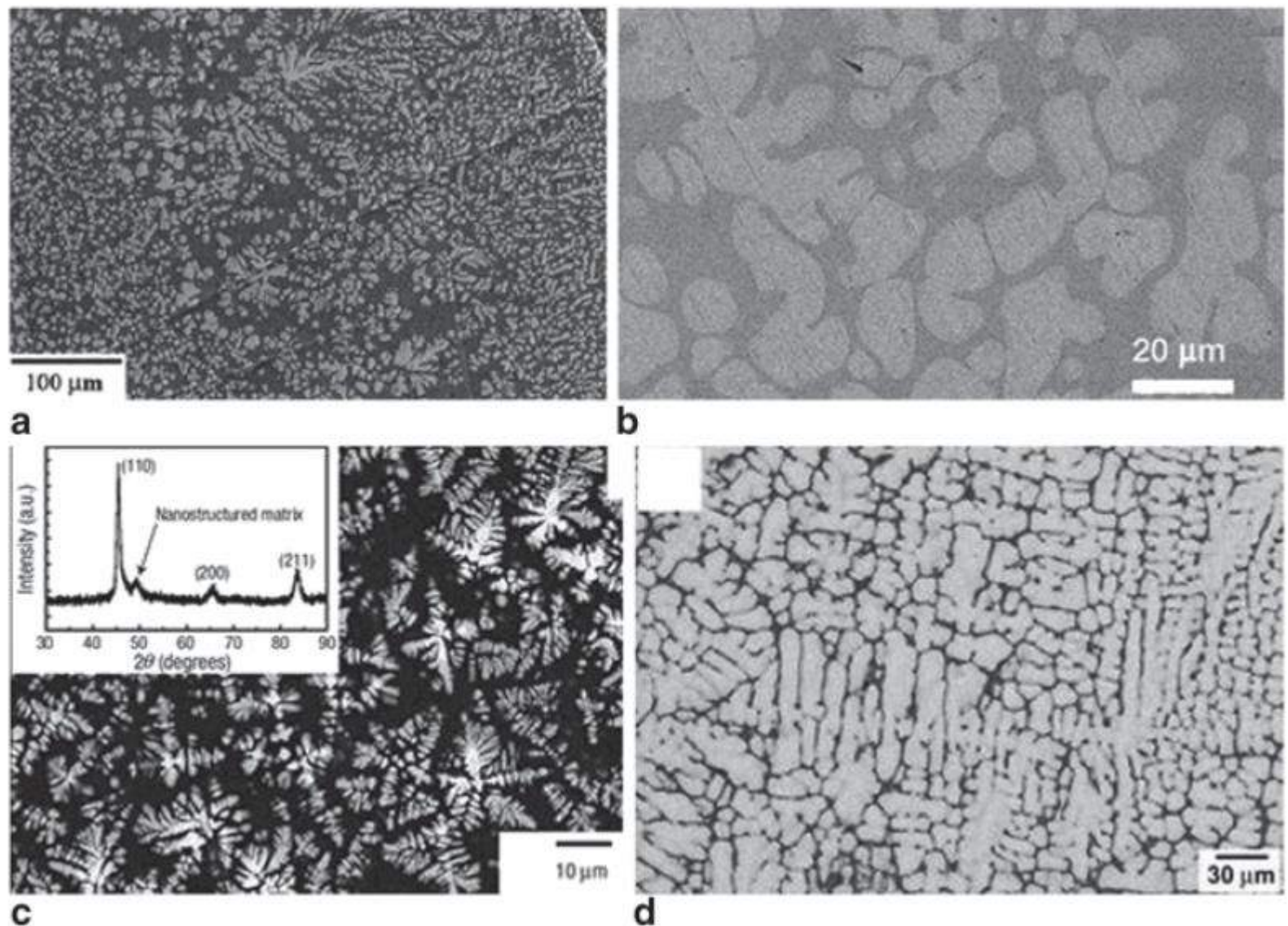


Simulated atomic configuration of glassy  $Zr_{66.7}Ni_{33.3}$  (extracted and reproduced with permission from [10] © 2010, Nature Publishing Group).



Structure of  $Ni_{81}B_{19}$  metallic glass obtained from an ab initio MD simulation (adapted with permission from [12] ©2009 Elsevier).





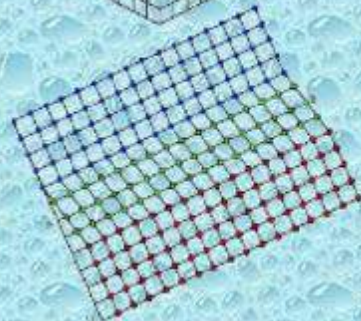
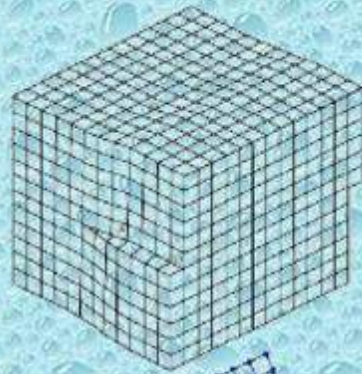
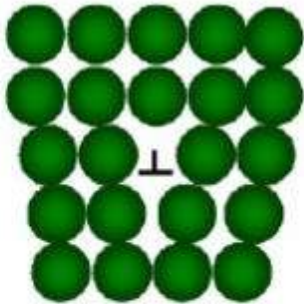
**Fig. 1.9** Microstructures of MG heterostructures that exhibit tensile ductility. Variation in spacing, size, and shape of the second phase dendrites is present in each sample. **a**  $(\text{Zr}_{75}\text{Ti}_{18.34}\text{Nb}_{6.66})_{75}\text{X}_{25}$ , **b**  $\text{Zr}_{39.6}\text{Ti}_{33.9}\text{Nb}_{7.6}\text{Cu}_{6.4}\text{Be}_{12.5}$ , **c**  $\text{Ti}_{60}\text{Cu}_{14}\text{Ni}_{12}\text{Sn}_4\text{Ta}_{10}$ , **d**  $\text{Ti}_{66.1}\text{Cu}_8\text{Ni}_{4.8}\text{Sn}_{7.2}\text{Nb}_{13.9}$  in situ composites



# STRUCTURAL PROPERTIES

- There is no grain boundaries and dislocations.

Edge dislocation



Grain boundary





## MECHANICAL PROPERTIES

- They have high corrosion resistance.
- They are very strong.
- They have high workability.
- They are highly ductile.

## ELECTRICAL PROPERTIES

- They have high electrical resistivity  $100 \mu\Omega \cdot \text{cm}$ .
- Temperature coefficient is zero or negative.
- Eddy current loss is very small.

## MAGNETIC PROPERTIES

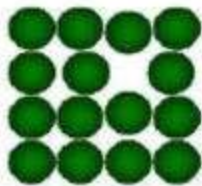
- They have soft and hard magnetic properties.
- They exhibit high saturation magnetisation.  
[ the amount of magnetic field that a magnet can produce is known as saturation magnetisation ] Strong magnets have higher saturation.
- The core loss is very less.
- They have narrow hysteresis loop.

## CHEMICAL PROPERTIES

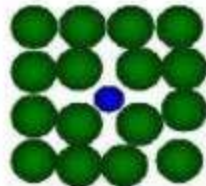
- They are highly reactive and stable.
- They can act as a catalyst.
- They have no crystalline defects.



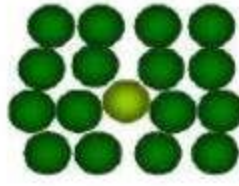
### Point defects of crystals



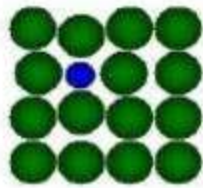
Vacancy



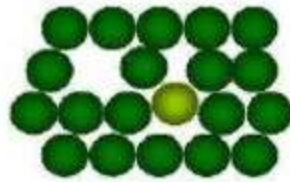
Interstitial impurity



Self-interstitial

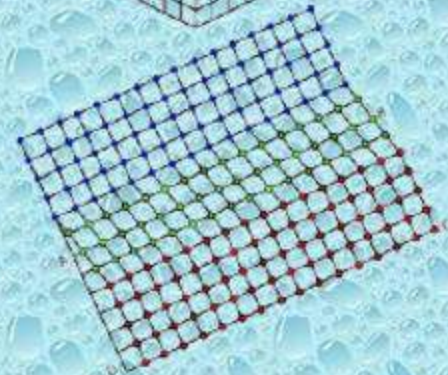
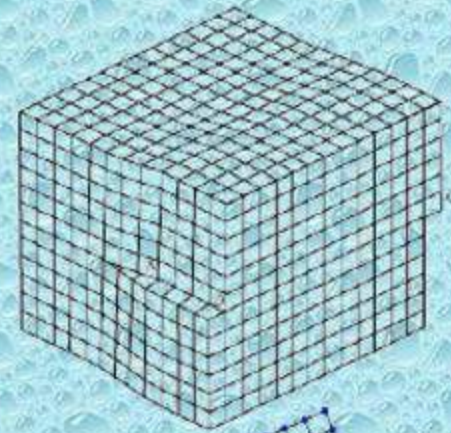
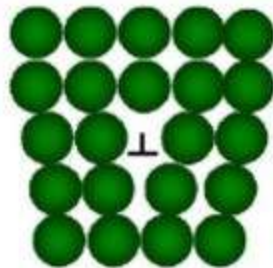


Substitution impurity



Frenkel defect

### Edge dislocation



## APPLICATIONS

- They are used as reinforcing elements.
- They are used to construct fly wheels.



- They are used to make razor blades and different kinds of springs.



- They are used in core of highpower transformers.



- They are used in tape recorder heads.





- **The metglass wires and ribbons are ideal for generating harmonics.**
- **They are used in producing high magnetic field for magnetic levitation effect.**
- **They are used to make standard resistance, computer memories and magnetic resistance sensors.**
- **They are useful for preparing container for nuclear waste disposal, magnets for fusion reactors.**

- They are ideal for making surgical instruments and implantation materials.



- <https://www.youtube.com/watch?v=oULkYytYPgs>

# Assignment

1. Cite the two common characteristic of glasses.
2. Why glass behave as brittle at room temperature ? What happen to the glass at high temperature?
3. Discuss briefly the heat treated process which involved in the manufacturing process of glass bottle
4. Differentiate in term of structures of materials:
  - Glass and glass-ceramic
  - Metal and metallic glass