Design of alumina bodies with directional porosity by a freeze-casting method

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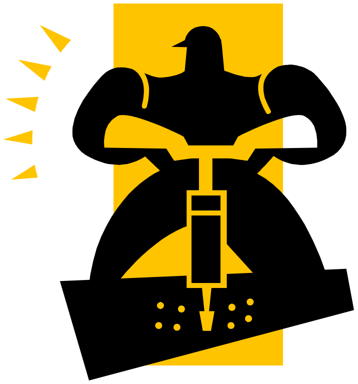
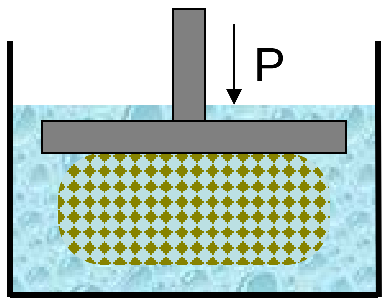
INTRODUCTION

MANUFACTURE OF POROUS MATERIALS

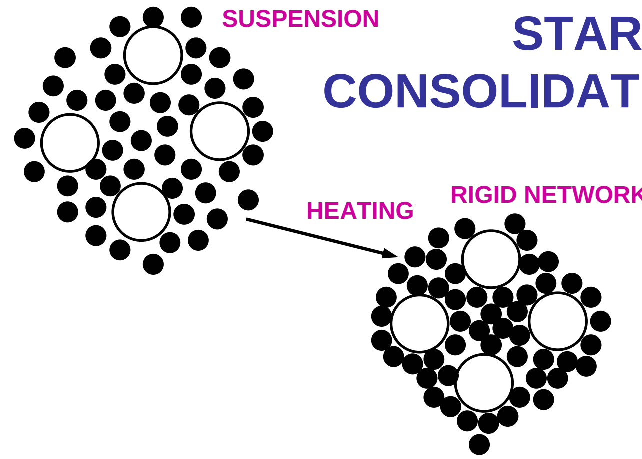
FIRST POSSIBILITY



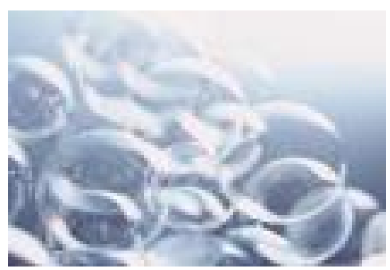
SPOUNGE IMPREGNATION



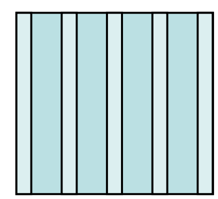
STARCH CONSOLIDATION



OTHER POSSIBILITY



FREEZE CASTING



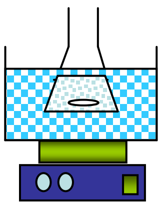
SOAP BUBBLES → **SURFACTANT**

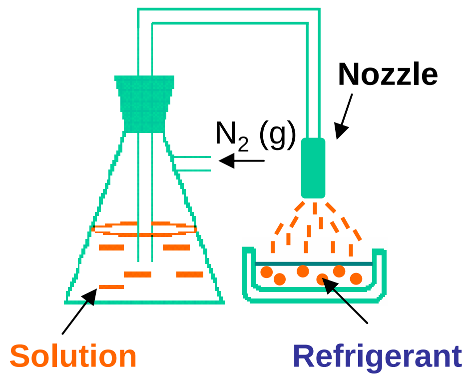
FREEZE-DRYING

Synthesis of nanopowders
Synthesis of mixed oxides
Synthesis of POROUS materials

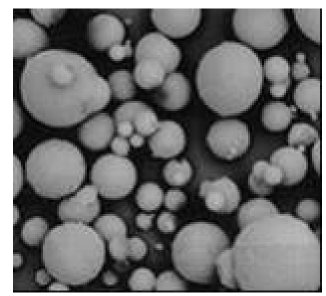
Solution → **Freezing** → **Freeze-Drying** → **Thermal treatment**

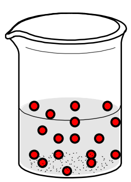
Vacuum sublimation at low T





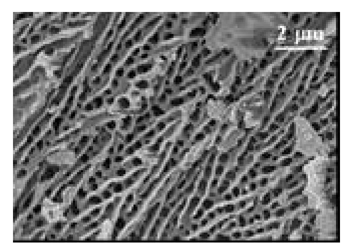
Porous, soft granules





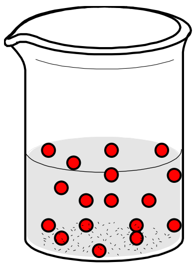
Shaping method

Suspension → **Freeze-Casting** → *Porous bodies*



FREEZE-CASTING

Suspensions



Organics $\xrightarrow[\text{Warm milling}]{\text{Camphene}}$ Sublimation at T_{room}

Aqueous $\xrightarrow{\text{Freezing}}$ Sublimation under vacuum (T < 0º C)

Ice formation and growth

Crystal size = f ($T_{freezing}$, additive)

CRYOPROTECTOR

FREEZE-CASTING

CRYOPROTECTOR

PVA

Glycerol

Decrease in $T_{freezing}$

10 wt% -1.6ºC
20 wt% -4.8ºC
30 wt% -9.5ºC

Interaction with dispersant forming micelles

Bonding to water molecules

Ice crystallization
Open microstructure
Higher homogeneity
Cracking avoiding
Increased strength

OBJECTIVE

PREPARATION OF ALUMINA BODIES WITH
ALIGNED POROSITY BY FREEZE-CASTING

Influence of the solid content of the starting suspension

Addition of glycerol as cryoprotector

Influence of freezing conditions

→

Pore size and distribution

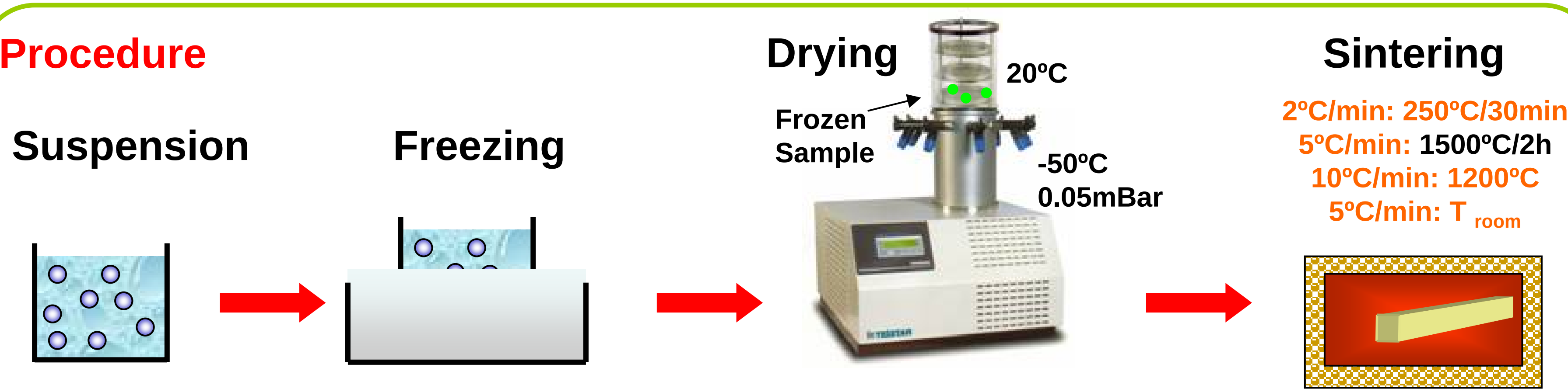
Microstructure

EXPERIMENTAL

Suspension

Al_2O_3 Condea HPA05 (USA), d_{50} = 0.35 μm, S_S=9.5 m^2/g
Dispersant: poly(acrylic acid, PAA (Duramax D3005, Rohm/Haas, USA)
Ball milling 6h
Cryoprotector, Glycerol

Procedure

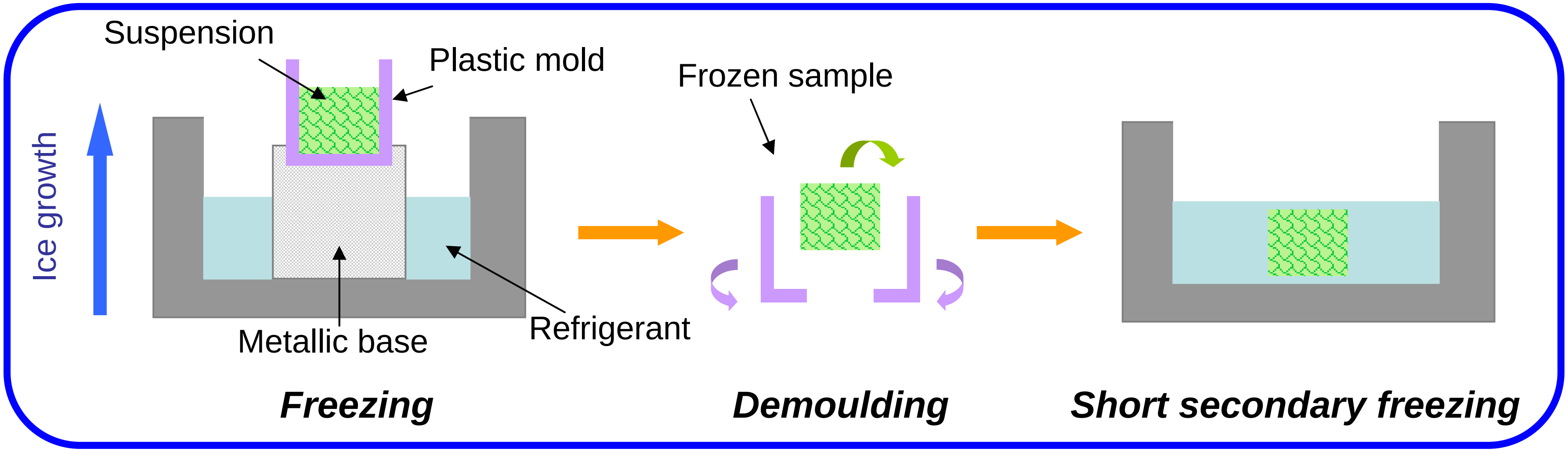


Characterization

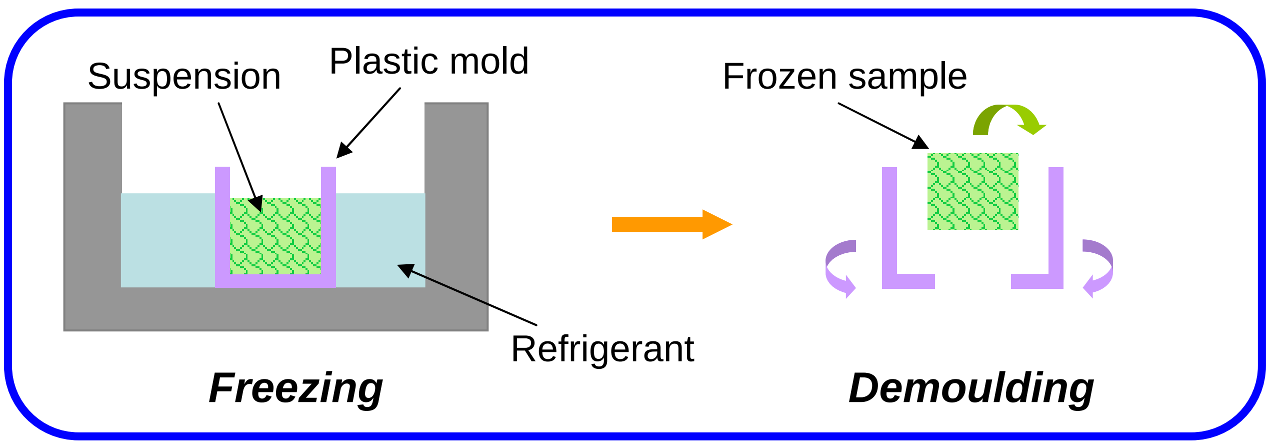
Flow behaviour (CR): Haake RS50 (sensor DC60/2)
FE-SEM
Mercury Intrusion Porosimetry
Green and sintered densities

EXPERIMENTAL

Directional Freezing



Bulk Freezing



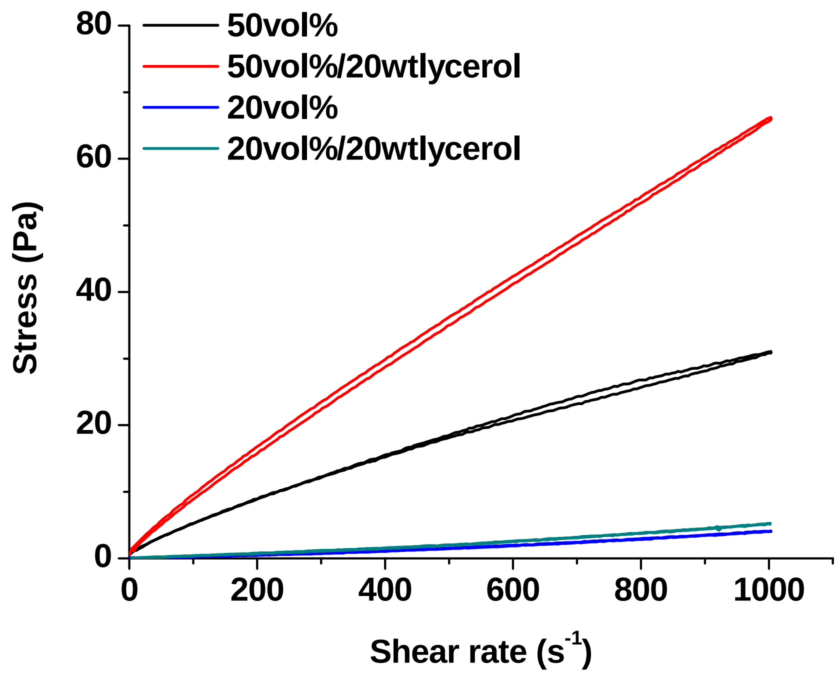
EXPERIMENTAL

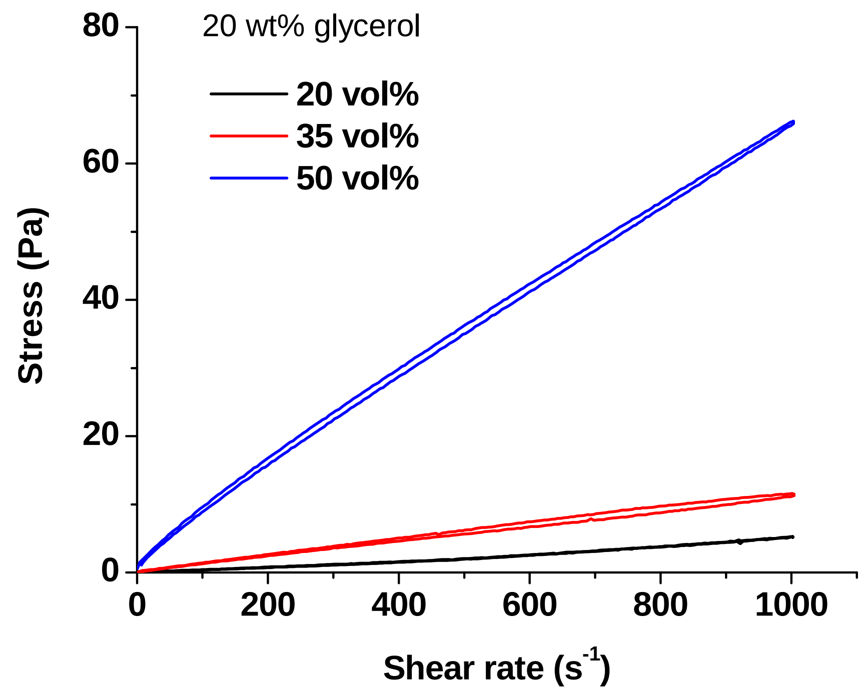
EXPERIMENTAL CONDITIONS

Solids content	**20, 35, 50 vol%** **50, 68, 80 wt%**
Cryoprotector (Glycerol)	**0, 10, 20 wt%** (respect to water)
Freezing device	**bulk** **directional**
Freezing rate	**N_2 (l)** (-198ºC) instantaneous **freezer** (-20ºC) slow

RHEOLOGY OF FREEZING SUSPENSIONS

EFFECT OF GLYCEROL AND SOLIDS LOADING





DIRECTIONAL FREEZE CASTING

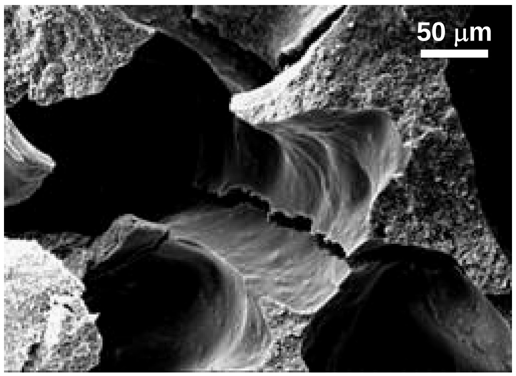
EFFECT OF SOLIDS CONTENT

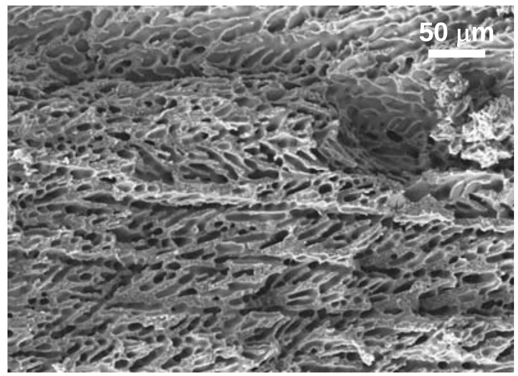
20 wt% glycerol

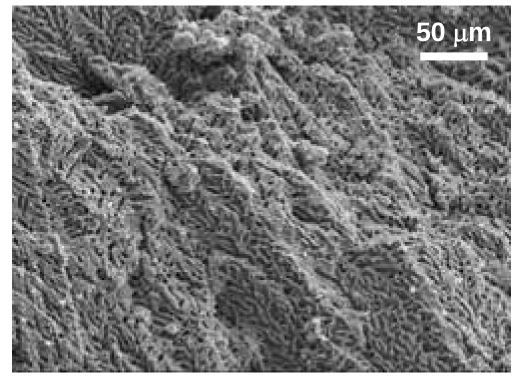
20 vol%

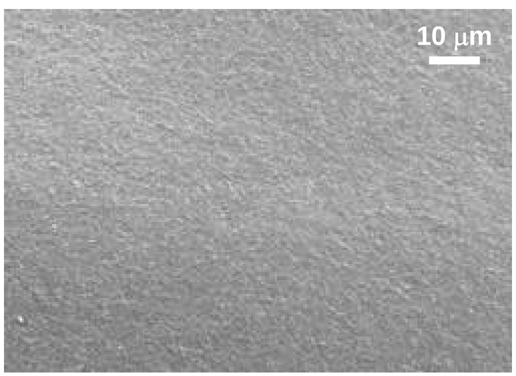
35 vol%

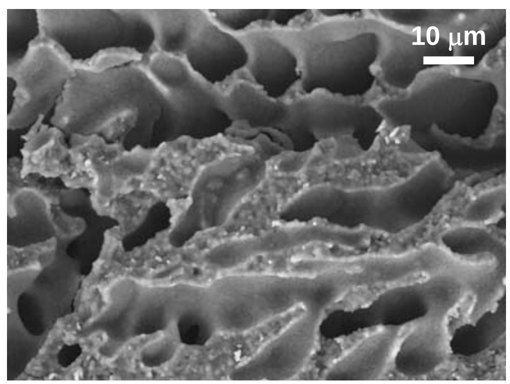
50 vol%

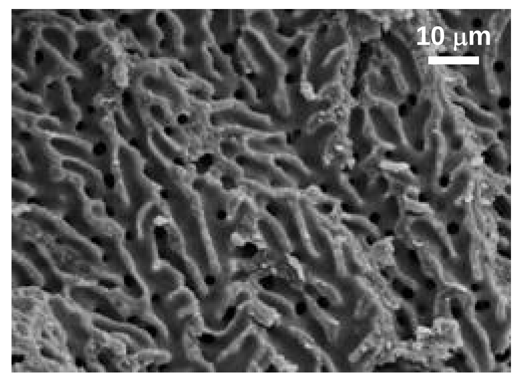








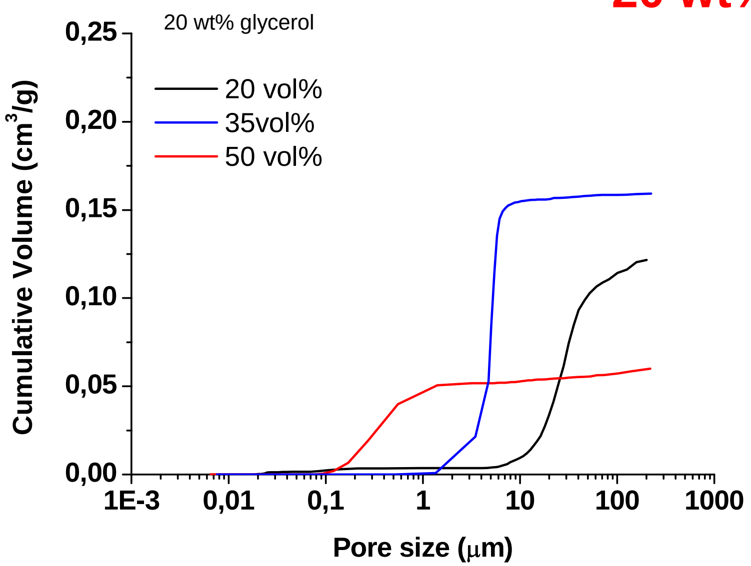


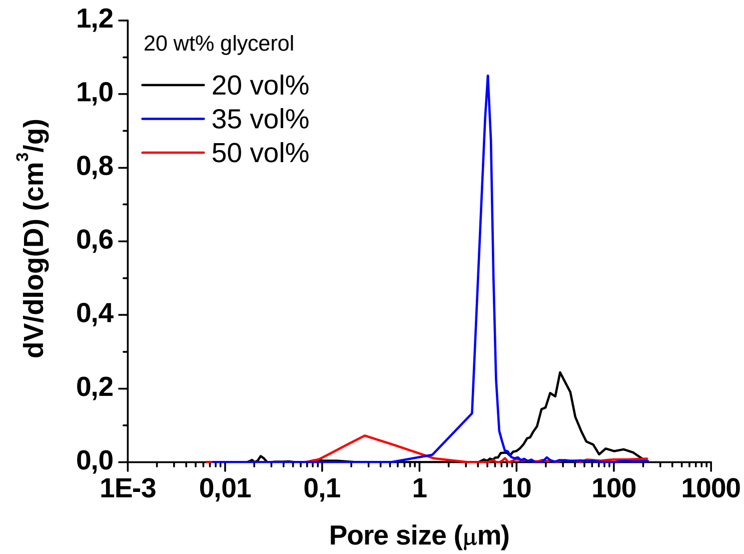


DIRECTIONAL FREEZE CASTING

EFFECT OF SOLIDS CONTENT

20 wt% glycerol





Properties of sintered bodies

Suspension (vol %)	*Relative density (% TD)*	*Porosity (%)*	
		Total	*Open*
20 vol%	47	53	29
35 vol%	58	42	30
50 vol%	78	22	10

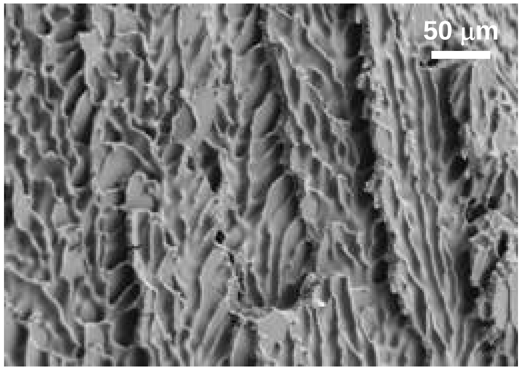
DIRECTIONAL FREEZE CASTING

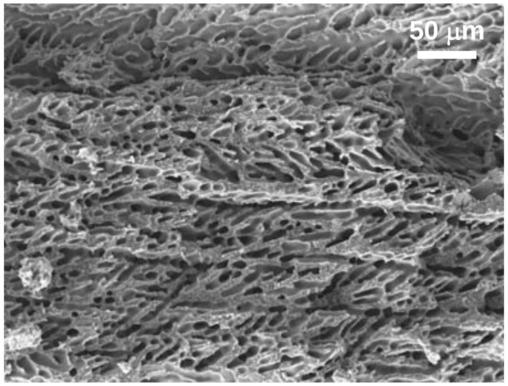
EFFECT OF CRYOPROTECTOR ADDITION

35 vol%

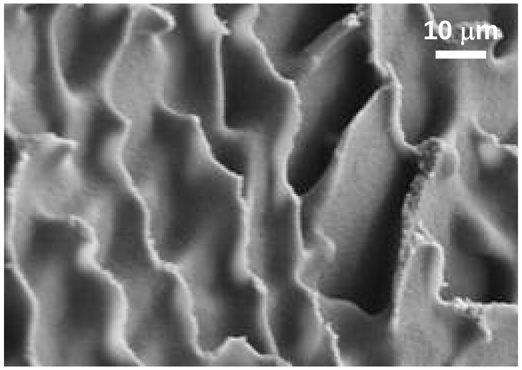
10 wt%

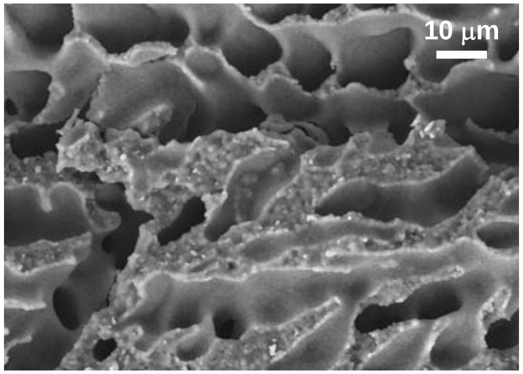
20 wt%





BETTER FORMATION OF CHANNELS

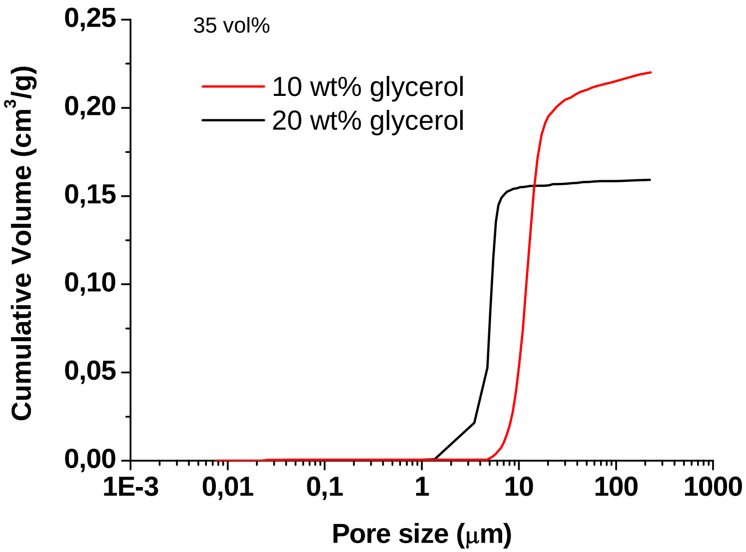


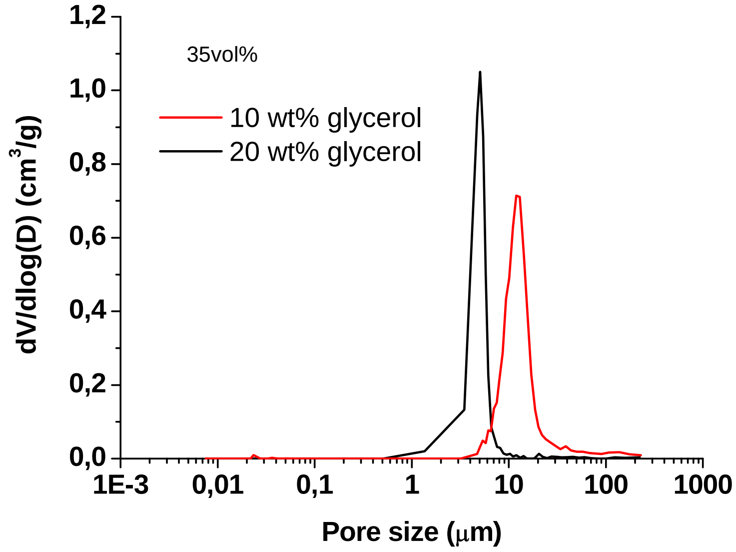


DIRECTIONAL FREEZE CASTING

EFFECT OF CRYOPROTECTOR ADDITION

35 vol%





Properties of sintered bodies

Glycerol (wt %)	Relative density (% TD)		Porosity (%)	
	Green	Sintered	Total	Open
10	31	55	45	42
20	39	58	42	30

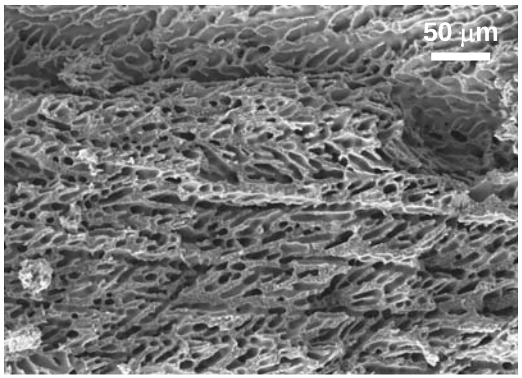
FREEZE CASTING

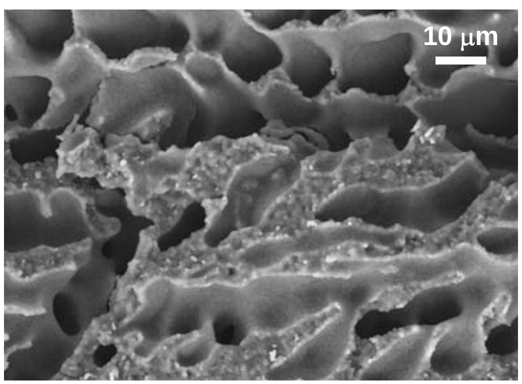
EFFECT OF FREEZING DEVICE

20 wt% glycerol

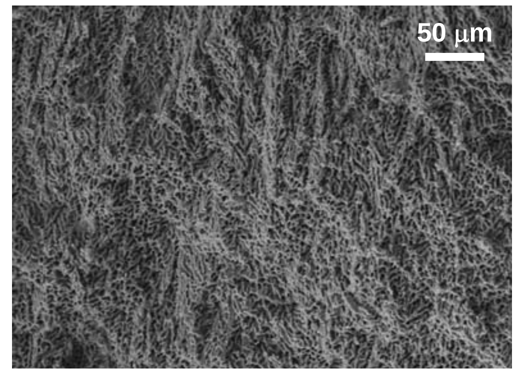
35vol%

Directional

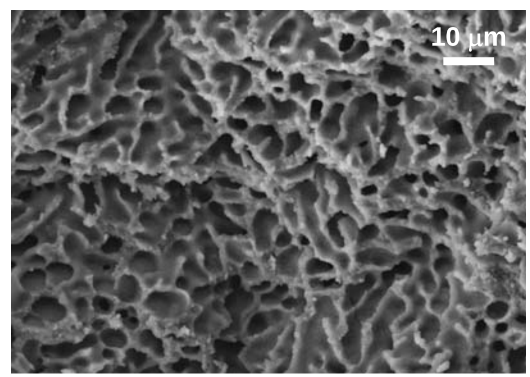




Bulk



NO PREFERRED ORIENTATION
LOWER PORE SIZE

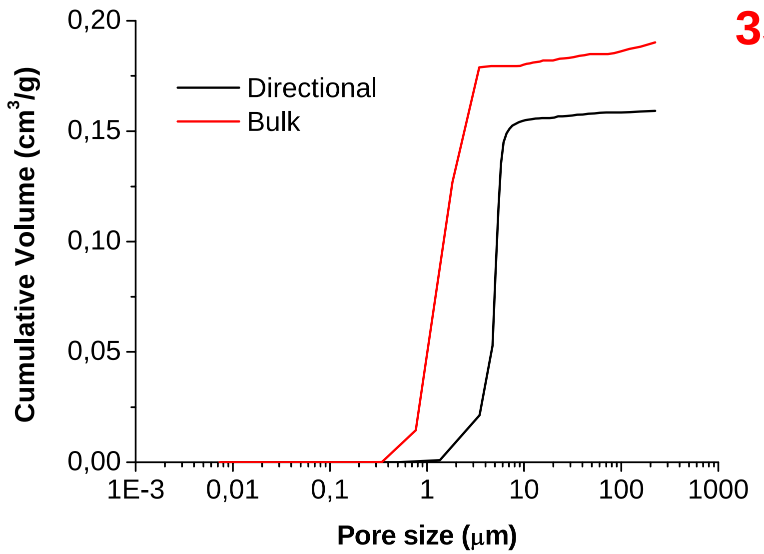


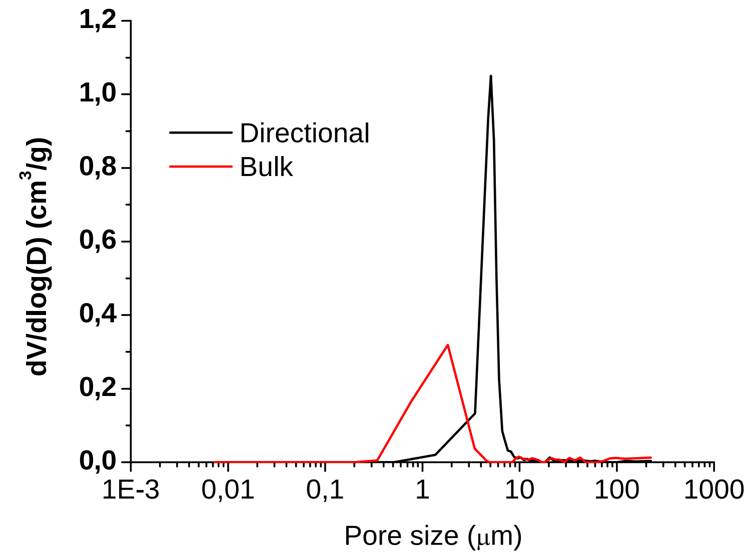
FREEZE CASTING

EFFECT OF FREEZING DEVICE

20 wt% glycerol

35vol%





Properties of sintered bodies

Freezing	*Relative density (% TD)*		*Porosity (%)*	
	Green	*Sintered*	*Total*	*Open*
Directional	39	58	42	30
Bulk	39	57	43	36

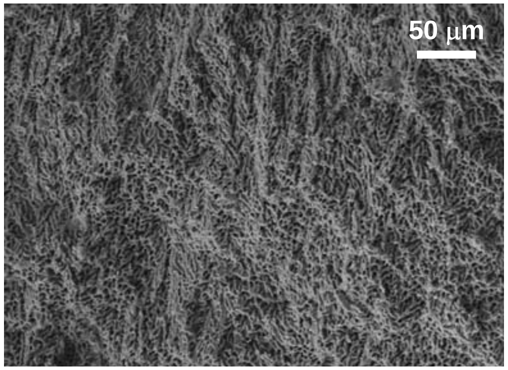
BULK FREEZE CASTING

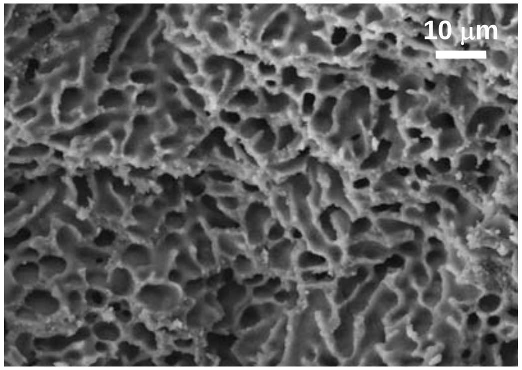
EFFECT OF FREEZING RATE

20 wt% glycerol

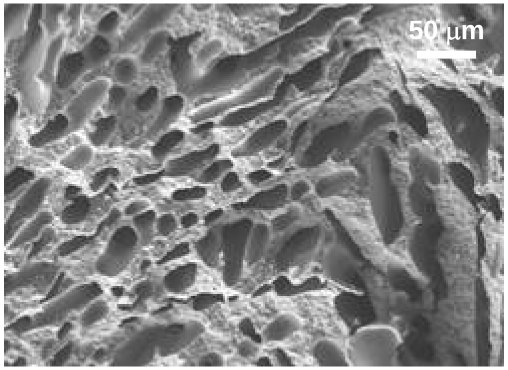
35vol%

Liquid nitrogen (-198ºC)

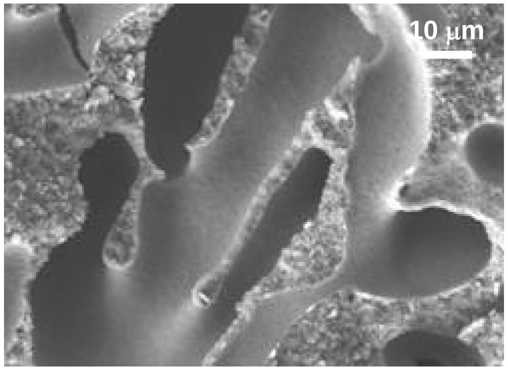




Freezer (-20ºC)



SLOWER RATE LEADS TO LARGER ICE CRYSTALS

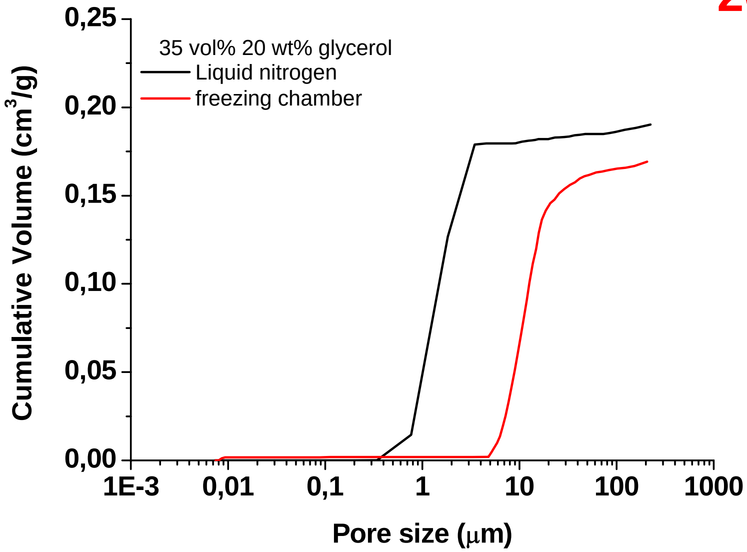


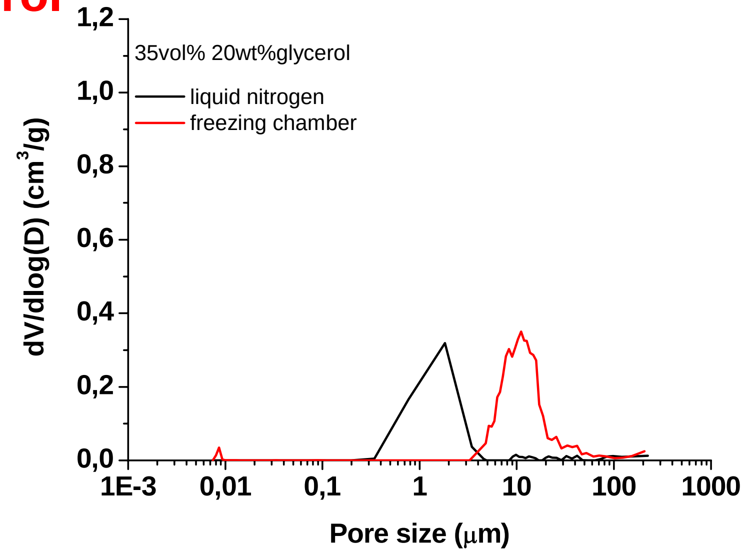
BULK FREEZE CASTING

EFFECT OF FREEZING RATE

20 wt% glycerol

35vol%

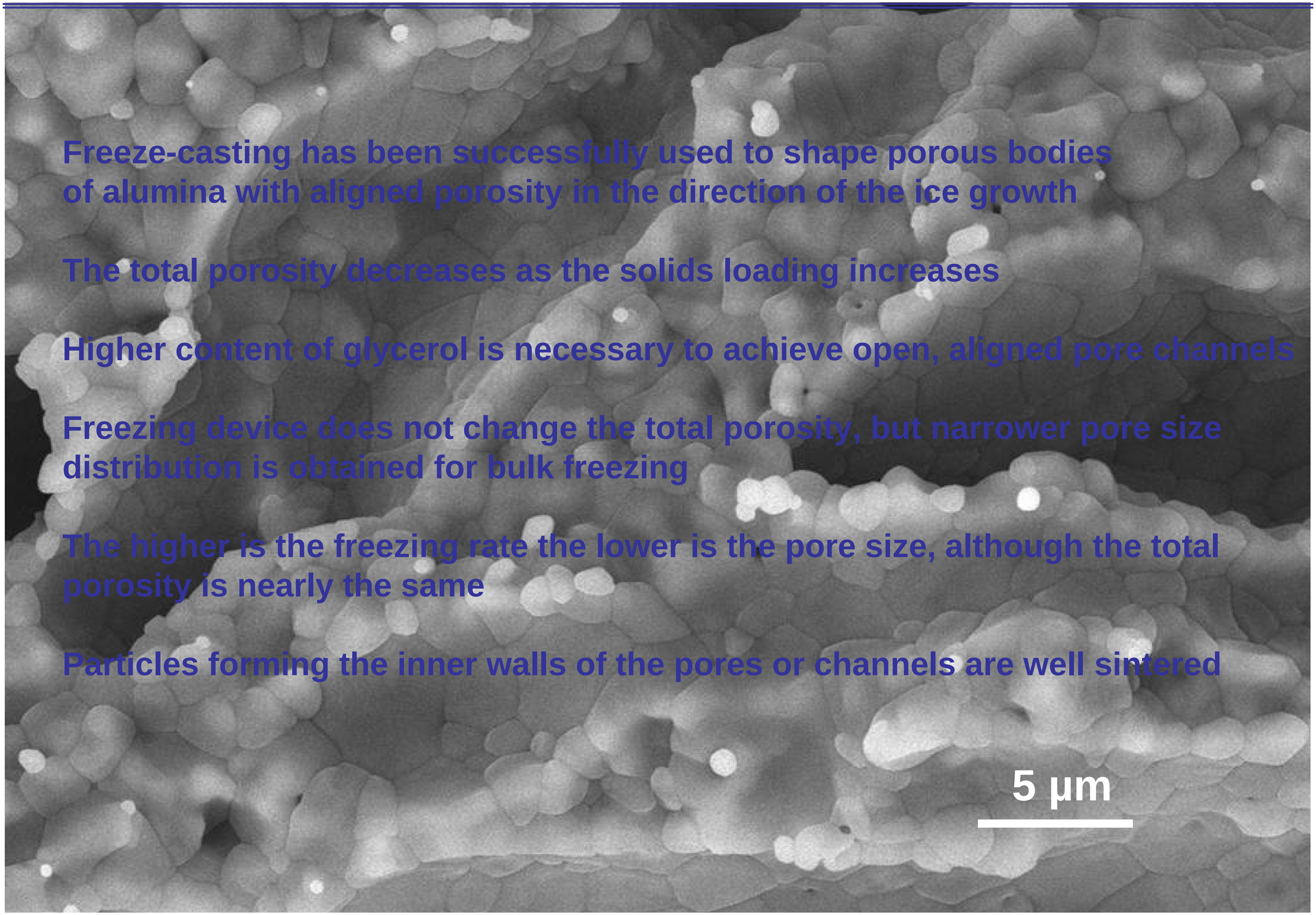




Properties of sintered bodies

Freezing	*Relative density (% TD)*		*Porosity (%)*	
	Green	*Sintered*	*Total*	*Open*
N_2-liq	39	57	43	36
Freezer	31	59	41	31

CONCLUSIONS



Freeze-casting has been successfully used to shape porous bodies of alumina with aligned porosity in the direction of the ice growth

The total porosity decreases as the solids loading increases

Higher content of glycerol is necessary to achieve open, aligned pore channels

Freezing device does not change the total porosity, but narrower pore size distribution is obtained for bulk freezing

The higher is the freezing rate the lower is the pore size, although the total porosity is nearly the same

Particles forming the inner walls of the pores or channels are well sintered

THANK YOU VERY MUCH