Progress in Additive Manufacturing (2022) 7:993–1008
https://doi.org/10.1007/s40964-022-00273-y

REVIEW ARTICLE

Sub-zero additive manufacturing: a review of peculiarities and applications of additive manufacturing at temperatures below 0 °C

Pushkar Kamble[1] · Rajendra Hodgir[1] · Gopal Gote[1] · Yash Mittal[1] · K. P. Karunakaran[1]

Received: 7 July 2021 / Accepted: 31 January 2022 / Published online: 18 February 2022

Abstract

Invariably all *Additive Manufacturing (AM)* processes occur in a narrowly controlled range of temperature and/or pressure. All established AM processes for metals and non-metals occur at ambient or higher temperatures. However, in recent years, AM processes are being developed for unique materials such as bio gels, medicines, colloids, aqueous solutions, etc., with lower working temperatures, sometimes even below 0 °C. Authors use the term Sub-Zero Additive Manufacturing (SZ-AM) for all such processes. The present review article gathers the work related to SZ-AM reported in recent years. This review article provides a bird-eye view of a wide range of applications and technical details of SZ-AM in numerous fields such as manufacturing, medicine, architecture, etc. The review helps to understand the challenges and the future scope of developing commercial SZ-AM machines. The case studies help determine the feasibility of using the SZ-AM process for unique materials for potential applications.

Keywords Sub-zero additive manufacturing · Cryogenic 3D printing · Bio-printing · Low temperature additive manufacturing

1 Introduction

Additive Manufacturing (AM) technology has grown out of its primary application for rapid prototyping [1]. AM industry predominantly uses metals, ceramics and polymers. Additively manufactured metal, polymer and ceramic parts are being used as functional products in various industries such as aerospace, automotive, prosthetics, infrastructure, energy devices and consumer goods. However, researchers are exploring non-conventional materials such as water [2], food items [3], ceramics, colloids, aqueous solutions and gels [4] for AM and related applications. These non-conventional materials require sub-zero process temperatures, unlike other established 3D printing technologies (Fig. 1).

The researchers have used various terms for specific applications of low-temperature AM processes such as Rapid Freeze Prototyping (RFP) [2], Ice 3D Printing [5, 6], Rapid Prototyping for ice parts [7], Cryogenic 3D Printing [8], Freeze-form Extrusion [9, 10], ice lithography [11], 3D Freeze Printing [4]. However, all such processes are referred to by the umbrella term "*Sub-Zero Additive Manufacturing (SZ-AM)* processes" in the present article. The present article summarizes all SZ-AM processes, their applications and the technological peculiarities that make them stand out from the conventional AM processes.

Sub-zero process temperatures demand a unique architecture incorporating a refrigeration system and a well-insulated workspace with protected motion and deposition systems. Therefore, process equipment for all such processes is different from its conventional counterparts. Also, the materials are different in SZ-AM processes than their traditional counterparts. Widely reported materials for SZ-AM are water and water-based solutions. A few groups also report ceramic slurries, food products, and hydrogels, but water is a predominant constituent (up to 90%) in all these materials. The flow properties of the materials such as viscosity, density and surface tension play a crucial role in determining the deposition methodology (Table 1).

✉ Pushkar Kamble
pushkarkamble@gmail.com

[1] Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai, India

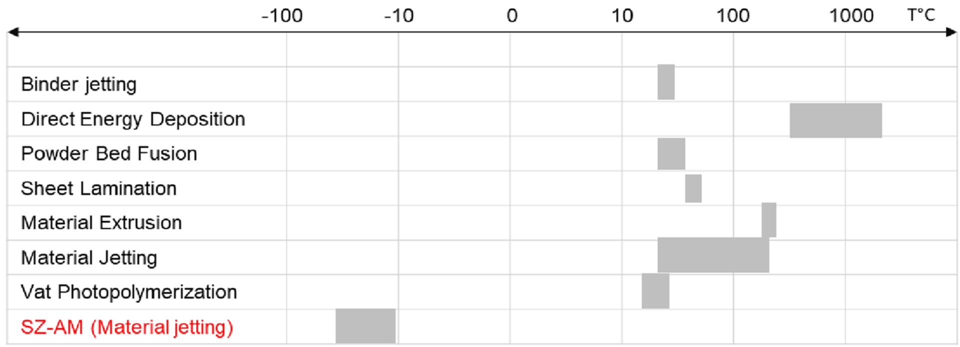


Fig. 1 Temperature Range of All 3DP Processes (Approximate)

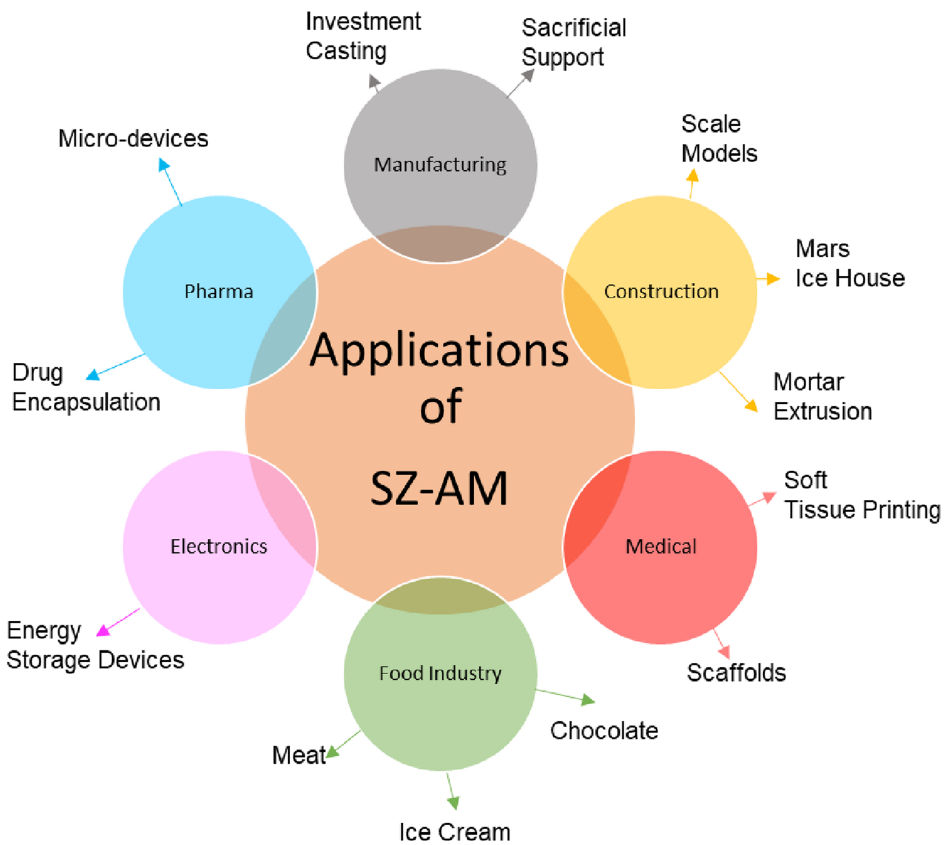


Fig. 2 Applications of SZ-AM

Table 1 Comparison of the SZ-AM Processes

Parameter	Extrusion	Single jet	Multi-jet
Multi-material capability in a single head	No	No	Yes
Resolution	Low	Moderate	High
Data Type	G-code	G-code	Rasterized Post Script File
Material Viscosity	High	Low	Low
Suitable Materials	Slurries, Meat, Dough, Gels, etc	Water, aqueous solutions, etc	Water, aqueous solutions, etc

2 Applications of SZ-AM processes

SZ-AM deals with a wide range of slurries and liquids; hence it has applications in several fields, as shown in Fig. 2. The applications and the related information are summarized in Table 2.

2.1 Manufacturing

Frozen AM products produced by SZ-AM technology are deployed in various manufacturing areas. Each of these areas is discussed briefly.

2.2 Investment casting

Additively manufactured ice parts are used as patterns for investment casting [12–14] in the place of wax (Fig. 3). M. C. Leu et al. have demonstrated using a single-jet ice 3D printer to produce the ice parts with a minimum resolution of 0.08 mm. AM ice patterns are maintained at sub-zero temperatures inside a freezer. An interface agent is spray-coated on the patterns that act as a barrier between the ice and slurry and helps retain the geometry. The slurry for making the mould contains the three components, viz., ceramic, binder and catalyst [13]. The slurry is prepared by mixing these components in the right proportion followed by cooling it to sub-zero temperatures.

After cooling to the right temperature, typically − 5 °C to 0 °C, the slurry is poured over the ice patterns in the mould flask [13]. It undergoes gelation and maintains its shape at sub-zero temperatures. As soon as the gelation is complete, the mould flask is taken out from the freezer and kept at room temperature. The ice pattern melts down as it comes to the room temperature along with the sprue and runners. Sprue and runners melt too, making a way to drain the water from the mould. The water is collected at the bottom (Fig. 4). The mould is then kept for drying in the open air. Once dry, it is sintered in the furnace at 800 °C, and subsequently the casting can be carried out as usual.

There are several benefits of replacing wax with ice. Wax tends to expand upon heating and melt during dewaxing,

Table 2 State-of-the-art of the SZ-AM Technology

Sl No	Material		Deposition	Temperature	Resolution	Application	Year	Reference
	Model	Support						
1	Water	Aqueous NaCl and dextrose solution	Single-jet deposition	− 20 °C	0.08 mm	Patterns for investment casting	2002	[15][63][54]
2	Water	Aqueous NaCl and KCl solutions	Single-jet deposition	− 20 °C	0.8 mm	Architectural models	2009	[37][64]
3	Ceramic	Methyl cellulose (10%)	Piston-based extrusion	− 10 °C	0.76 mm	Ceramic parts manufacturing	2014	[9][10]
4	Pharmaceutical drugs	–	Multi-jet deposition	− 30 °C	0.1 mm	Drug encapsulation	2015	[5]
5	Liquid metal alloys	–	Syringe-based extrusion	0 °C	0.045 mm	Flexible electronics	2016	[24]
6	Ice	-	Spray deposition	-	> 5 mm*	Ice sculptures	2017	[23]
7	Biogels	–	Syringe-based extrusion	− 78 °C	0.1 mm**	Tissue scaffolds	2017	[8] [25] [26] [28][30] [65]
8	Graphene aerogel	Water	Syringe-based extrusion	− 25 °C	0.04 mm	Energy devices	2017	[48]
9	Resin	Water	Custom dispensing	− 22 °C	Not available	Highly removable support for the resin parts	2017	[18]
10	Meat	–	Screw-based extrusion	0–5 °C	Not available	Custom food	2019	[34]
11	Water	–	Single-jet deposition	− 30 °C	0.03 mm	Micro-scale structures for microfluidic devices	2020	[21]
12	Water	–	Multi-jet deposition	− 25 °C	0.06 mm	Patterns for investment casting	2021	[61]

*Approximate value based on the images, not mentioned in the literature

**Based on the limited literature study

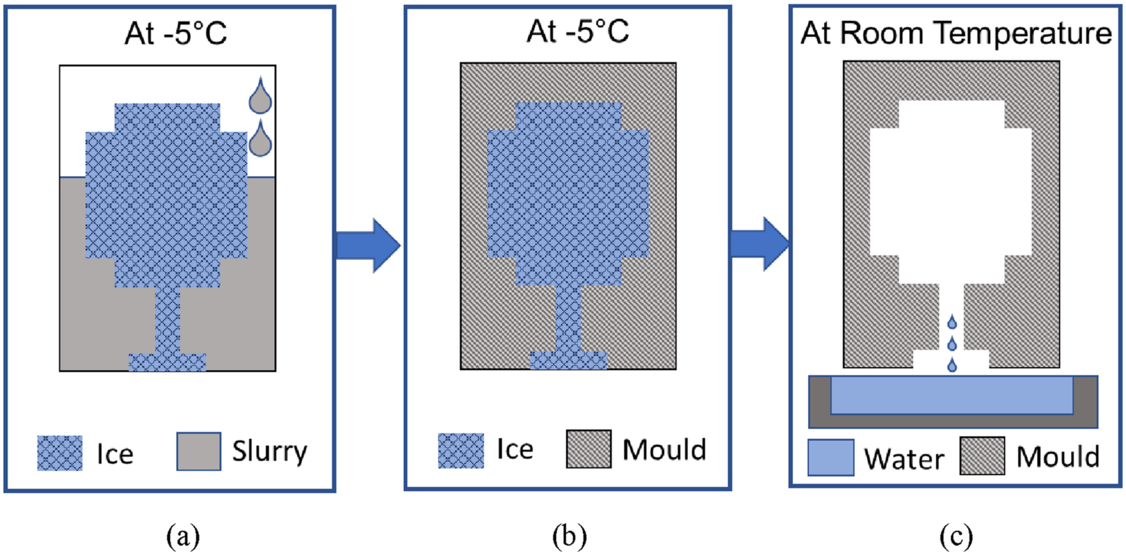


Fig. 3 Mould Preparation from Ice Pattern, (**a**) slurry being poured around the ice pattern inside the flask, (**b**) the slurry is made to undergo freezing at − 5 °C (**c**) The temperature of the flask is slowly increased to room temperature, which melts the ice pattern and mould is obtained

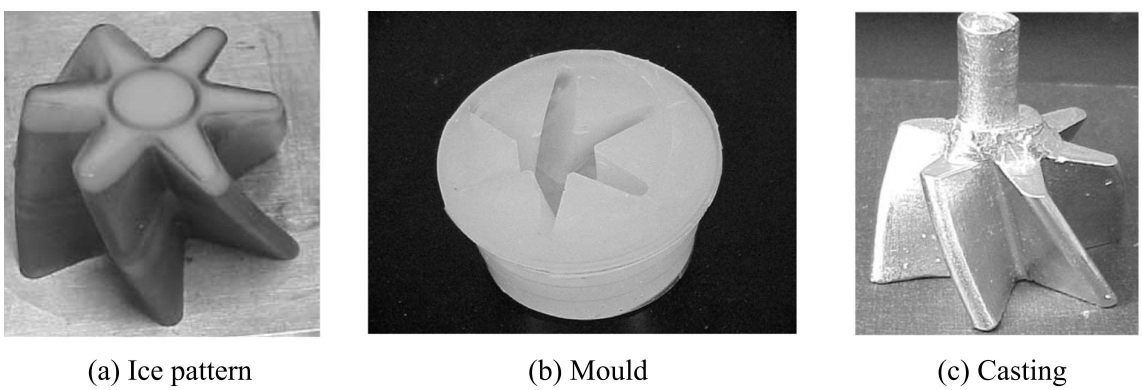


Fig. 4 Ice Investment Casting [15]

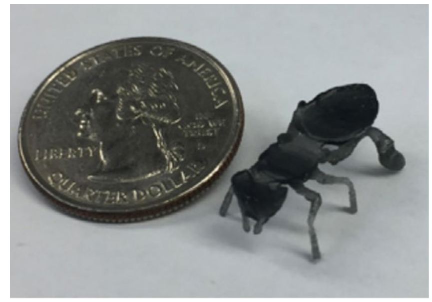
adding to the cracking tendency of ceramic moulds. On the contrary, ice contracts upon melting and reduces the mould cracking tendency [16]. Dewaxing and firing of the mould burn the wax, releasing harmful hydrocarbons into the air. Ice leaves the mould without any trace and is environmentally friendly [17].

2.3 Support material for polymer AM

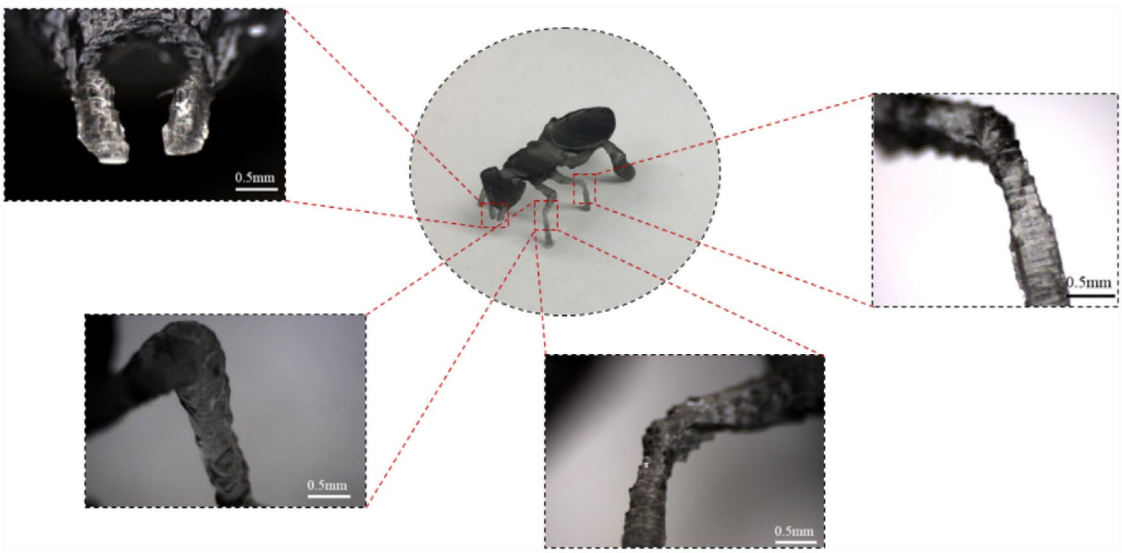
Ice serves as an excellent support material for photopolymer-based 3D printing processes [18]. The photopolymer and water are deposited selectively on the cold substrate using separate deposition heads. The deposition head is incorporated with the light source for polymerization. The process takes place at sub-zero temperatures. The water freezes into ice and acts as a support material. Light source cures the model photopolymer material. As soon as the part is completely manufactured, it is maintained at room temperature that melts away the ice and the polymer object is obtained. The water from melted support is discarded, and the polymer object is dried in the air. Figure 5b shows the model of an ant made of resin with water as a support material (Fig. 5a) where the minimum part dimension achieved is less than 0.5 mm (Fig. 5c) [19].

Presently, the support structure of the polymeric parts is removed mechanically, which sometimes results in the uprooting and damaging the surface of the part. Hence the ice support is helpful for the miniature polymeric parts to avoid a cumbersome support removal process. It also reduces the wastage of the precious polymeric material for support structure as it is usually discarded after use.

(a) Water and Polymer Printing



(b) Finished Product after Melting Water



(c) Dimensions

Fig. 5 Ice as a Support Material for the Photopolymer 3D Printing [18]

2.4 Micro-scale ice models

A single-jet piezoelectric nozzle-based system is used for making micro-scale models of ice without any support structure (Fig. 6a). The maximum height of the micro-scale structures is reported as 200 µm. The resolution of the process is 0.03 mm. Single nozzle deposits the micro-droplets that undergo freezing (Fig. 6b). The droplet size is varied by varying the frequency of the piezoelectric nozzle.

The droplets are sequentially deposited on the previously frozen structure. It means the previous droplet needs to be frozen entirely and reached to sufficient sub-zero temperature for the next droplet to be deposited. Therefore, a delay is given invariably in all AM processes for one layer to consolidate before printing another. This delay in the layers affects the quality of the printed part [20]. It is experimentally found that the droplet freezing time ranges from 50 to 300 ms, based on the droplet size. Therefore, a maximum delay of 300 ms is given for each droplet printing.

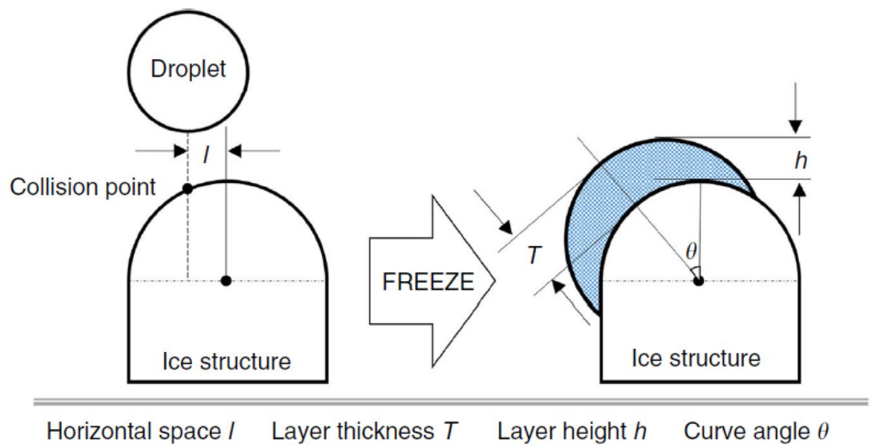
This process has a potential application in microfluidic device fabrication where the micro-scale ice structures can function as templates [6, 21].

2.5 Ceramic AM

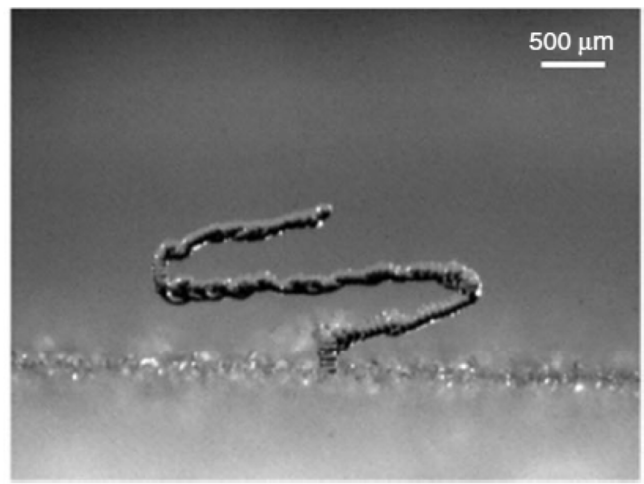
Ceramic parts are made by extrusion of the slurries through the nozzle similar to Fused Deposition Modelling (FDM) process. Usually, the deformation is observed for the large or thin parts since the ceramic slurries are made to have low viscosity for easy deposition; hence, they have low green strength. Moreover, they tend to dry slowly due to high water contents.

Hence, the ceramic slurries are extruded at low temperatures. As soon they are deposited, the water in the slurries freezes and turns solid. It strengthens to the previously printed layers, and they retain the shape until the process

Fig. 6 Micro-scale Structures Produced by Single-jet Sub-zero AM Process [6]



(a) Schematic diagram



(b) Micro-scale structure

completes. This process is called freeze-extrusion. Aqueous colloidal slurries of the ceramic materials are freeze-extruded at − 10 °C. A 10% methylcellulose solution is used as a sacrificial support material. The 3D-printed part of the ceramic is later sintered. The minimum resolution obtained by this process is 0.76 mm [9, 10].

2.6 Ice-based Electron-Beam Lithography (iEBL)

All established additive manufacturing processes can produce the parts with the resolution in the range of a few micrometres. For nanoscale structures, there are limitations to the existing AM processes. Ice electron beam lithography technique can produce geometries with a high resolution (nanoscale) along with flexible material selection. In ice-based electron beam lithography, the water vapour is released on the substrate maintained around − 140 °C (130 K) to form a thin film of ice. The thin film of ice is amorphous due to the condensation of water in the droplet forms [11]. The *Electron Beam (EB)* removes the ice as per the required geometry and exposes the substrate. As soon as the EB interacts with the ice film in the required pattern, the part of the film vanishes quickly. The phenomenon of ice removal is not yet much clear; however, Ding Zhao et al. (2019) claim that the removal of ice occurs by electron-stimulated reactions occurring due to radiolytic properties of EB [11].

The exposed part of the substrate is metallized, and the remaining ice is removed by dipping the substrate in the alcohol (Fig. 7). The process continues for the subsequent layer. The electron beam is useful here since it instantly removes the ice layer with sharp corners [11, 22]. The cryo-stage is maintained at 130 K throughout the process. Therefore, there are no thermal stresses involved; hence no warpage/cracking of the part is observed.

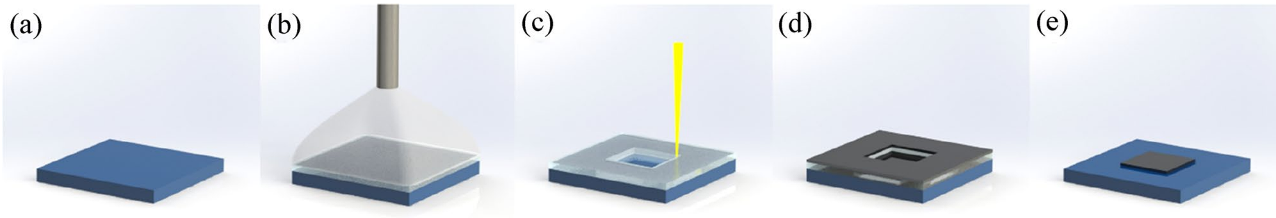


Fig. 7 Ice-based Electron-Beam Lithography (iEBL) [22], (**a**) cryo-stage maintained at 130 K, (**b**) water vapour being condensed and solidified on the cryo-stage (**c**) concentrated EB being used to remove the portion of the ice film (**d**) metallization of the ice film (**e**) ice film removed. (Reprinted with permission from Yu Hong, Ding Zhao, Dongli Liu, et al., *Three-Dimensional* in Situ *Electron-Beam Lithography Using Water Ice*, Nano Letters, Copyright 2018, American Chemical Society)

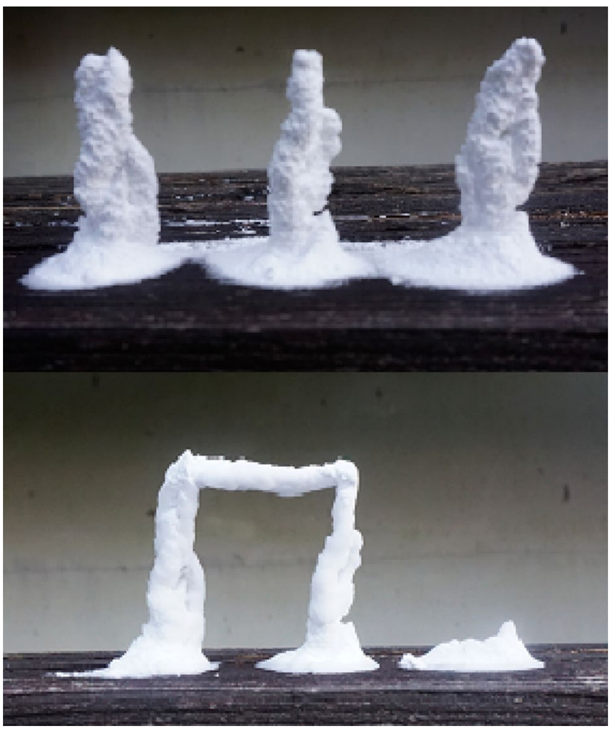


Fig. 8 Ice Jet 3D printing [23]

2.7 Ice spray printing

Ice spray printing directly jets the atomized ice particles from the nozzle. The nozzle can be mounted on the motion system to create the desired geometry (Fig. 8). A servo-motor operated spray jet deposits the ice on the cold substrate. 3D printed pillar-like structure of ice has been demonstrated [23]. The technique of ice spray can be used for creating ice sculptures. Ice melts readily; thus, the 3D-printed ice parts are recyclable and do not create waste compared to plastics. Although the resolution of the process is low, i.e., approximately up to 5 mm, it may be further improved with better spraying and control strategies.

2.8 Freeze-printing of alloys

Freeze-printing of alloys is an interesting application of the SZ-AM. With the advent of flexible devices, the need for manufacturing methods of flexible electronics arises. The flexible electronics are dependent on the metallic networks embedded in the polymeric substrates. A novel technique of alloy freeze-printing allows fabricating the flexible polymeric parts with an embedded network of liquid metals (Fig. 9). The metals such as Indium-Gallium eutectic alloy are liquid at room temperature. The liquid metals are deposited in a layered manner on the cold substrate at 0 °C. As the metal is dispensed from the nozzle, it solidifies and imparts the structural rigidity for the overhanging features. The metallic structure is subsequently encapsulated in the crosslinked elastomeric matrix, and the temperature of the part is raised to ambient temperature. It retains the metal at a melted state embedded inside the elastomeric matrix, and the flexible conductive channels can be fabricated (Fig. 9). The minimum feature size obtained by this process is 0.45 mm [24].

2.9 Biomaterial 3D printing

Biomaterials are the ideal materials for the SZ-AM process. Biomaterials are generally hydrogels, biocompatible colloids and mixtures. The AM parts made of biomaterials are used as scaffolds for tissue growth. Sometimes, the solutions containing live tissues are also printed for organ printing.

2.9.1 Hydrogels

Composite hydrogels mimic the structure of the soft tissue. AM can accurately reproduce the complex shapes of the biological geometries. Prosthetics and implants can be mass-customized to provide the tailored size and shape according to the receiver's needs. It has been shown that the super-soft gel 3D printed structures made from polyvinyl alcohol and phytagel mimic the stiffness exhibited by the soft tissues

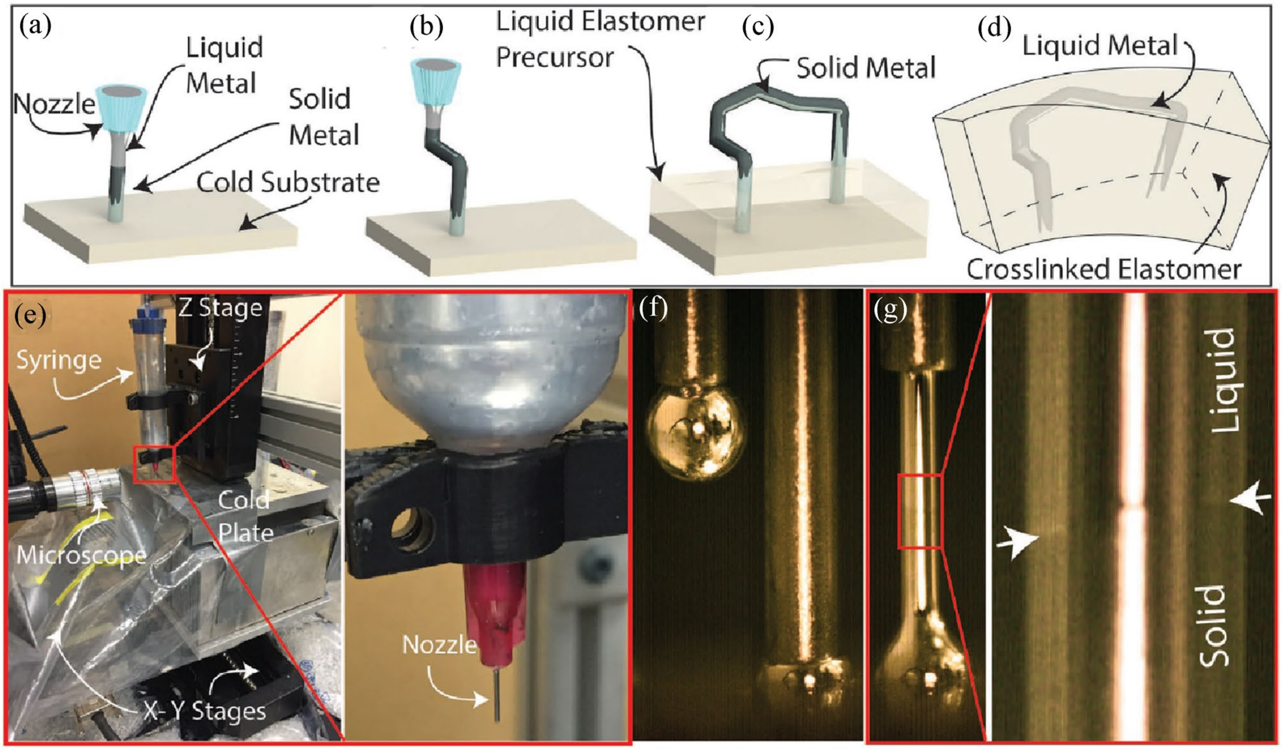
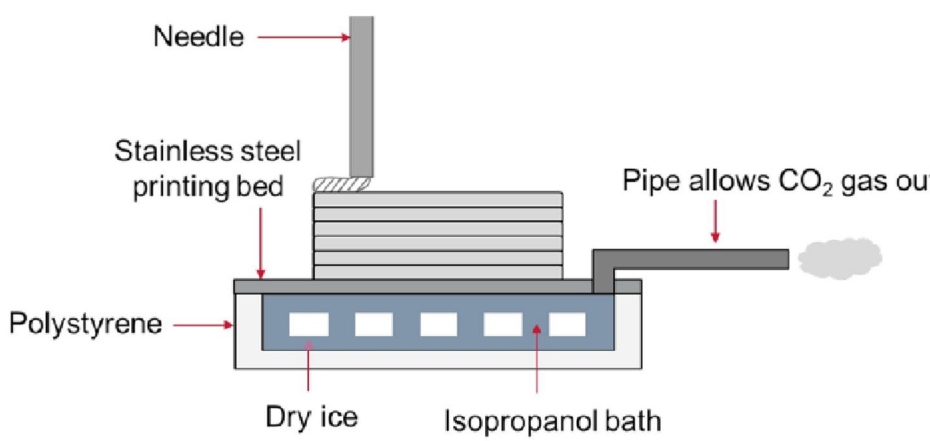


Fig. 9 Freeze Printing of the Metallic Materials [24], (**a**) Room-temperature liquid metals such as Indium-Gallium eutectic alloy (melting point:15.7 °C) is deposited on the sub-zero surface (**b**) solidified metal structure is created on the sub-zero surface (**c**) elastomeric precursor is poured on the metallic structure (**d**) the part is brought to the room temperature which melts the metal embedded in the flexible elastomeric matrix (**e**) experimental setup of alloy freeze-printing with nozzle (**f**) initial droplet and droplet-substrate contact (**g**) solid–liquid interface propagation in vertical printing

Fig. 10 Cryogenic 3D Printing Setup for Hydrogel 3D Printing [8]



such as the brain and lungs [8]. A stainless-steel stage is used to print the hydrogels, and the stage is cooled using the isopropanol and solid CO_2 bath that provides the required temperatures up to -80 °C. Isopropanol helps to distribute the temperature throughout the stainless-steel stage equally. Figure 10 shows the schematic diagram of the experimental setup. The needle deposits the material layer by layer on the cold substrate of stainless steel. The structures up to 20 mm height are printed using this setup.

Syringe-based extrusion of the agar gel and water (40 g/l) is an exciting finding [25]. In this experiment, the deposition of the hydrogel material is done on a cold surface, but it is located inside a closed flask. With the deposition of each layer, the cooling liquid is also released in the flask around the layer such that the layer is half immersed in the cooling

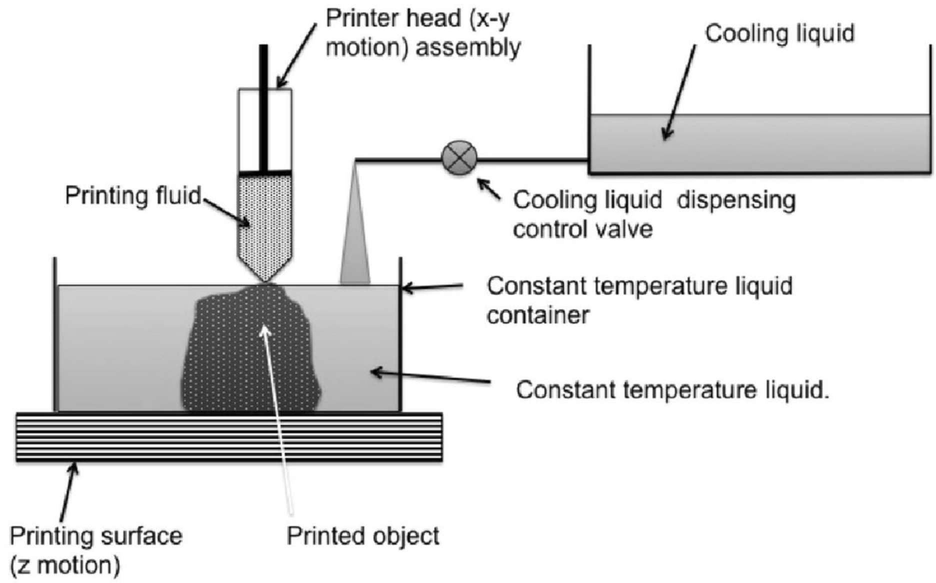


Fig. 11 Hydrogel AM inside a cooling liquid bath [25]

liquid (Fig. 11). It provides the rapid and uniform cooling of the material.

Cellulose nanocrystals (CNCs), xyloglucan (XG), Polycaprolactone, Bone morphogenic protein-2 loaded calcium phosphate nanoparticle and poly (L-lactic) acid are cryogenically 3D printed using a similar extrusion-based technique on the cold stage, but the cooling liquid bath is not used [26–28].

2.9.2 Hollow tubular structures

AM enables the fabrication of the hydrogel-based scaffolds structure for tissue growth. However, the scaffold structure needs to have structural complexity and suitable surface properties to allow the bone tissues to regenerate and integrate with the scaffolds. Enhanced vasculature and osseointegration help in faster and better recoveries from bone defects [29]. Hollow tubular structures provide the best solution for bone tissue regeneration and blood vessel structure development. SZ-AM allows the fabrication of the hollow tubular structures for the scaffolds. Hollow tubular scaffolds enable rapid osseointegration. Gelatin-methacryloyl (GelMA) is used for the fabrication of such scaffolds. GelMA is a semi-synthetic hydrogel that enables the cell cultivation environment. A syringe-based extrusion setup is used to deposit material on a cold substrate at -5 °C [30]. The benefit of using SZ-AM over other AM processes for hollow tubular structures is that the SZ-AM can precisely control the directional growth of the crystal structure of the ice, which helps in getting a uniform and hierarchical size distribution of the pattern.

2.9.3 Porous structures with hierarchical pore size

The freeze-fresh technique is a novel technique that produces the scaffold structure with hierarchical pore sizes, such as nanoscale, microscale and macroscale [31]. Hierarchical pore size provides the sites for better osseointgration. The freeze-fresh technique uses extrusion, to print the structures at room temperatures, frozen and freeze-dried later and crosslinked. It creates a mesh of the pores of varying pore sizes.

As shown in Fig. 12, the alginate ink is deposited on the substrate. A gelatin bath is used for supporting the soft and flexible print structure. Alginate gel is a biocompatible material used as a scaffold for cell growth. The printed structure is then frozen and lyophilized. In lyophilization, the structure is exposed to low temperature and high vacuum, sublimating the water content. After lyophilization, the part is submerged in the calcium chloride ($CaCl_2$) solution. Calcium chloride dissolves the gelatin and helps in crosslinking of alginate. The alginate part is then submerged in the cell culture, which helps in cell growth on the printed scaffold structure.

2.10 Food industry

3D printing is gaining popularity in the food industry since it increases the aesthetic value of food items. Also, AM provides tailor-made and well-engineered food items with proportionate ingredients for enhanced palatability. In the cryogenic food 3D printing technique, the food item is extruded from the nozzle [32], and it is submerged partially in the cryogenic fluid so that the layer being printed is always at a predetermined distance from the surface of the fluid. It helps

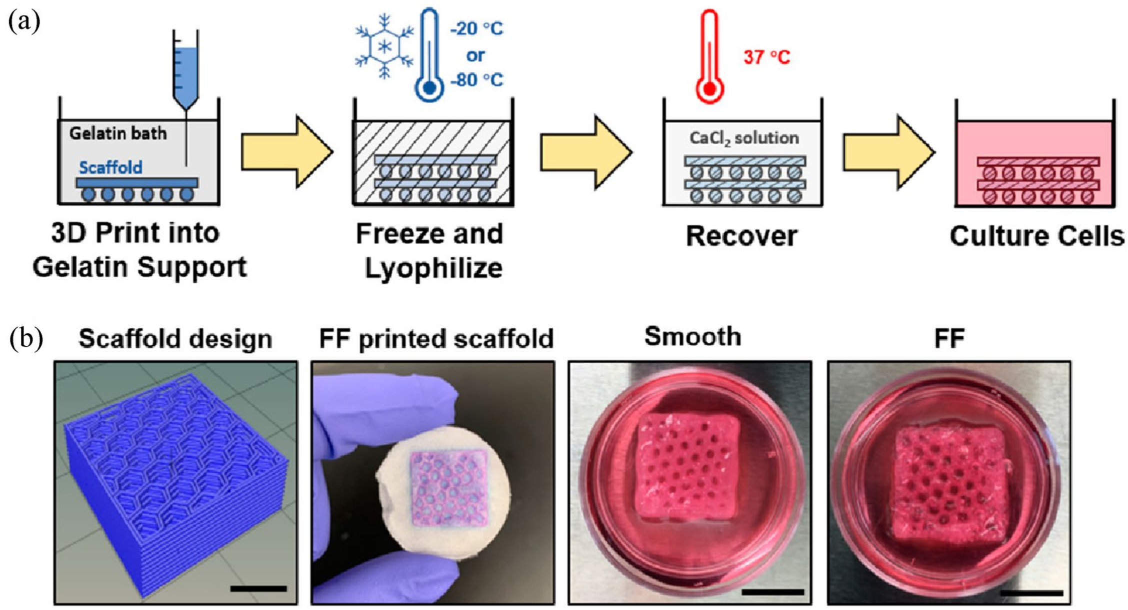


Fig. 12 Freeze Fresh Technique [31], (**a**) Alginate ink (biocompatible get) is 3D printed using a syringe and a needle inside a gelatin bath that provides structural support; it is frozen and freeze-dried at − 20 °C/− 80 °C (lyophilized) to remove the water content followed by dipping in calcium chloride (CaCl2) solution at 37 °C, which dissolves gelatin and crosslinks the alginate, creating the scaffold which is then used for cell culture, (**b**) The process of making porous scaffold from CAD to cell culture

in the directional cooling of the material, which enhances the crystal stricture of the ice and the food quality [33].

2.10.1 Meats

Slurries of fibrous meats are 3D printed at temperatures lower than 4 °C. The meat slurries are extruded from the nozzles in the required shapes. The screw-based extrusion method gives the best results compared to the syringe-based and inkjet-based methods. The screw-based extrusion also enables the proper mixing of the fibrous meat slurry. Slurries of other food items such as garlic, salt and fats are deposited in between the meat layers for additional flavour and palatability [34]

2.10.2 Ice creams and chocolates

Robots in Gastronomy is a group that works on implementing technology in the art of making food. Luis E. Fraguada et al. of Robots in Gastronomy have demonstrated using a 3D printer to create food items such as ice creams and chocolates [35]. They use a flash-freezer named Anti-Griddle from Polyscience that has a build plate that can cool up to − 34 °C. It is ideal for ice creams and pulpy foods like chocolates [36]. The ice creams and pulpy food items are deposited using a syringe-type extruder.

2.11 Construction

SZ-AM is also used in the field of architecture and the construction industry. Ice is an easily available environment-friendly material. Also, it readily melts and can be reused when left at room temperature without creating any waste products. Hence it is proposed to be the best material to create the scale models of the buildings as a reference and 3D visualization.

2.11.1 Architecture of phase change

The architecture of phase change is the term coined by Prof. Pieter Sijkpes of McGill University. Ice is demonstrated as a material to produce the scale models of the buildings [18]. A retrofitted FDM printer makes the ice 3D printed architectural shapes [37] with specialized toolpath planning [38].

2.11.2 Mars ice house

As a part of the contest at NASA, ice is proposed as a candidate material for creating the habitat on Mars. Ice is transparent, abundantly available on Mars and easy to work with. Ice provides insulation against the frigid Martian environment. It is easy to create ice structures using 3D printers [39].

2.11.3 Cementitious materials and Mortar 3D Printing

Cementitious materials are possible to be 3D printed using inkjet printing (binder jetting) [40], SLS or extrusion [41–43]; however, slurry extrusion may be more suitable for SZ-AM since it helps in maintaining the printed slurry shape by freezing it and gives stability to the structure as mentioned in section Ceramic AM. Similarly, *Self-Compacting Concrete (SSC)* has good flow properties and does not require any external vibrations for consolidation [44]. Therefore, the SZ-AM process may be suitable for its deposition.

2.11.4 Pharma

In the pharma industry, there is a requirement for various chemical assay kits to assess the properties of the drugs. Lab-on-chip is an innovative device that integrates several laboratory functions on a small-sized chip. Several miniature devices perform complex chemical processes through the network of microchannels, sensors, and electrical circuits. All such devices need the manufacturing of microchannels. Existing microchannel fabrication processes through photolithography are meticulous and time-taking.

2.11.5 Microfluidics array chips

SZ-AM allows the faster and easier production of microfluidics-based assay kits and drug delivery devices. The 3D-printed ice structures play the role of templates. First, cold photopolymers are poured over the 3D printed microscale ice templates and cured using light. Later, the ice is melted out to produce the microfluidic channels in the polymeric matrix [5].

2.11.6 Drug encapsulation

Several medicines are a combination of more than two drugs. The proportion of the drugs varies as per the dosage and needs to be accurate. SZ-AM helps make the drugs with tailor-made composition. The inkjet printhead deposits the drug solution as per the required quantity on the cold surface of encapsulation material. The drug solution undergoes freezing and solidification as soon as it is deposited on the cold surface. Multi-jet printhead allows the printing of multiple drugs as per the requirement. After the printing is complete, the encapsulation material is spread over the 3D printed rigid structures of the drugs that solidify. After that, the encapsulated drugs are harvested and packaged [45].

2.11.7 3D Nano-printing for electronic devices

Various electronic devices such as batteries and supercapacitors are widely used in various products. These devices are always optimized for the maximum energy content and power to weight ratio. An emerging technique called *Freeze Nano Printing (FNP)* is used to fabricate devices that allow complex structures and high energy density.

Graphene Aerogels (GA) are the lightest structures with high energy density and strength. The aqueous solution of the GA (0.5 mg/ml) is deposited with the help of the piezoelectric nozzle on the cold substrate at − 20 °C. Then, the GA solution undergoes freezing. Ice is used as a support material. Once the structure is fully printed, it is maintained at − 190 °C in a liquid nitrogen bath for the ice crystallization (Fig. 13). Further, it is freeze-dried to sublimate the ice content, and the GA parts are retrieved [46, 47].

The low concentration of the GA in the aqueous solution enables hierarchical porous structures. Additionally, freeze drying and further reduction by post-processing with high temperature enable the least dense structures. The GA structures made by the FNP technique are noted in the Guinness world record for the least dense 3D printed structures [48].

3 Architecture of the SZ-AM machines

SZ-AM processes require low temperatures; hence it is essential to note the differences in the architecture of SZ-AM machines. SZ-AM processes can be classified into two categories based on their style of deposition head, such as extrusion-based and liquid jet-based (Fig. 14). The extrusion process either uses a screw or a syringe-type extrusion mechanism. The jet-based process uses either single jet or multi-jet dispensing.

It is a general observation that the multi-jet printheads used for aqueous solution use piezoelectric actuation. They are robust and can handle a wide range of liquids since only mechanical actuation is involved. However, thermal printheads have lower life than piezoelectric printheads and are very sensitive to the contents of the ink since a part of the ink undergoes phase change during deposition.

3.1 Extrusion-based system

Extrusion-based systems are largely used for gels and slurries. The bio gels are extruded using the syringes since they need great precision. Piston-cylinder arrangements extrude the ceramics due to high pressures generated to extrude even the highly viscous slurries. The screw-based extrusion is used for ceramics at a room temperature extrusion purposes [49, 50]. Research published by Shakor et al. (2020) provides information on the extrusion of the mortar for construction

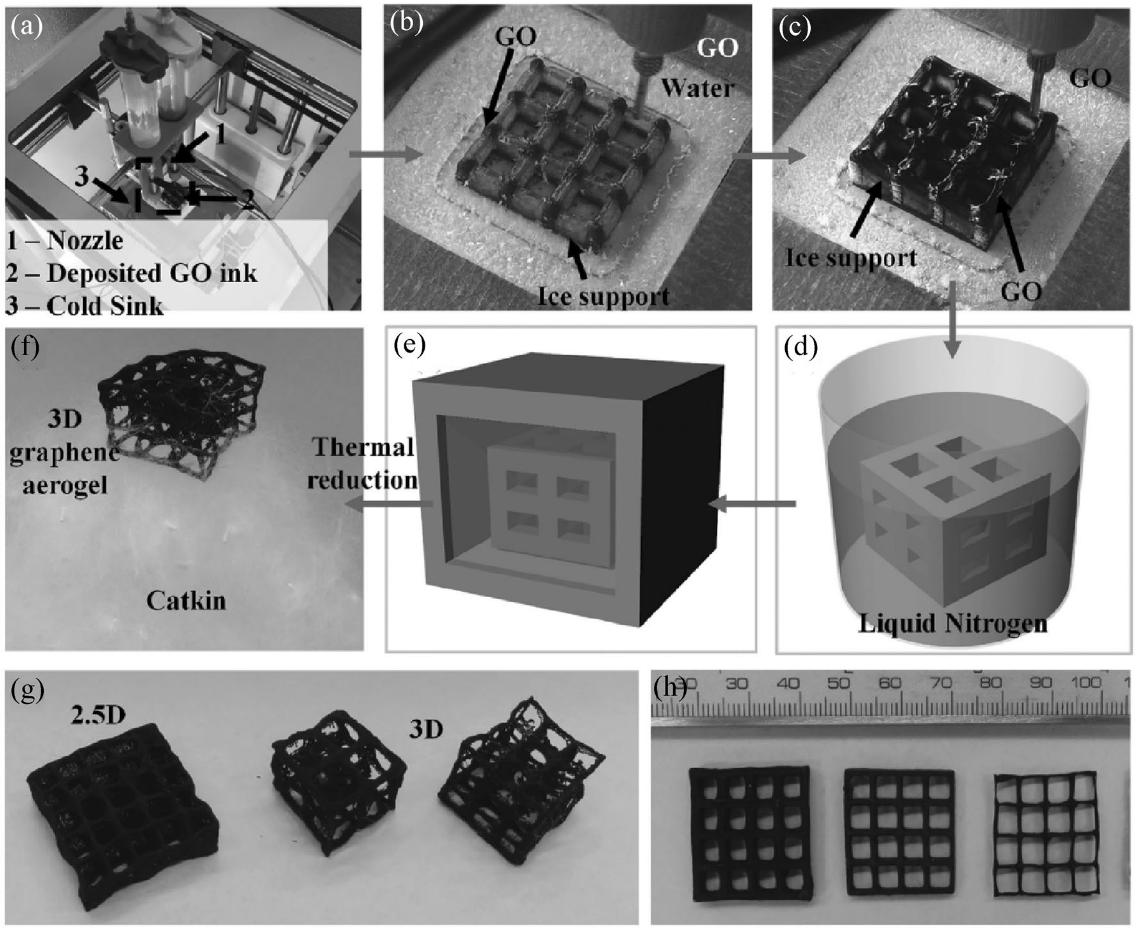


Fig. 13 Graphene Oxide Structures Produced by Sub-zero AM Process [47], (**a**) 3D printing set up (**b**) 3D printing of ice support with *Graphene Oxide (GO)* as part material (**c**) 3D printing of GO suspension (**d**) immersing the 3D printed part in liquid nitrogen (**e**) freeze drying to sublimate the water content and obtain dry GO part (**f**) the final ultra-light part placed on a catkin flower to appreciate its low weight (**g**) 3D parts made of GA (**f**) parts with various part thicknesses

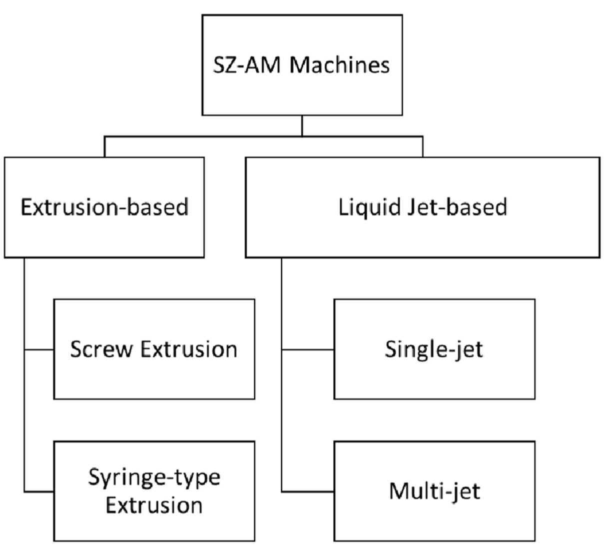


Fig. 14 Classification of the Sub-zero AM Processes

purposes [42]. Implementation of low-temperature deposition and freezing of slurry provide better structural stability to the printed structure. It can be slowly brought to room temperature as it cures.

For slurry-based materials and food items such as meats are extruded using the screw-based extruders since the screw enables uniform mixing of the ingredients of the slurry mixtures. However, more research is required for the screw-based extruders since some studies suggest that piston-based extruders are better for food due to highly viscous material [51].

The extrusion process uses a ram that pushes the piston in the cylinder [10]. The ram is pushed using the screw driven by the stepper motor. In the screw-feeder type extrusion system, the screw is continuously used for the material transport to the nozzle. The build time of the part is dependent on the extrusion rate. The extrusion rate is directly proportional to the force applied by the extrusion ram and the fluid viscosity. Viscous fluids need more force for extrusion.

Usually, the work platform or substrate is cooled using liquid nitrogen, solid CO_2 or a Peltier cooler. In some processes, where the part heights are more than 5 mm, the cooling liquid is filled around the printed part. In some processes, the insulated work chamber is maintained at sub-zero temperature.

3.2 Liquid jet-based system

Liquid jet-based systems are classified based on the type of the dispensing head as a single and multi-jet-based system.

3.3 Single-jet dispensing

For ice 3D printing, the single-jet system is primarily used to handle liquids with a wide range of viscosity and surface tension. Water and aqueous solutions have comparatively low viscosity. A miniature piezoelectric valve is operated with the help of the voltage waveform and manoeuvred with the help of the g-codes. It helps to precisely deposit the droplet of the liquid only where it is required, known as the drop-on-demand technique [2].

A single-jet system has a deposition, motion, and freezing systems. The deposition system consists of a piezoelectric-based nozzle that ejects the droplets as per requirement. The voltage pulse is fed to the nozzle, activating the piezoelectric actuation to eject the droplet [15]. The workspace is maintained at sub-zero temperatures using liquid nitrogen and a refrigeration system [7][52].

There are two adjustable parameters in a single-jet system that affect the quality of the 3D printed part. The parameters are water feed rate f and the scan speed v, i.e. the speed of the motion system. The water feed rate depends on the pressure P and the nozzle diameter d. The quality of the part can be measured in terms of layer thickness, line width [53] and surface roughness [54]. The layer thickness can be varied by altering the water feed rate and scan speed. The surface roughness varies with change in the f and v. To predict the surface roughness theoretically; the water droplets are modelled as hemispheres. Hemispherical droplet models are used for surface roughness and layer height prediction [55]. Apart from that, there is another model where the droplets are assumed to coalesce before freezing, giving a continuous layer of water. The model is used to predict the layer thickness and surface roughness [54].

In the single jet and multi-jet deposition-based processes, the material's phase change is involved. The liquid is deposited on the cold surface and is consequently frozen. Hence it is crucial to determine the freezing time of each layer before the subsequent layer is deposited. Thermal models are developed for the SZ-AM processes based on the waterline method for pure water [56] and an aqueous solution of salt or dextrose [57]. It is found that the solidification time between the two successive layers is 0.7 s when the layer thickness is between 0.1 and 0.15 mm. As the layer thickness goes on increasing, the solidification time increases too.

Support material selection for the SZ-AM processes is challenging. The support material for the frozen liquids such as water and aqueous solutions should be immiscible with water, have the same contact angle with the water, and be chemically inert and removable easily from the ice structures. Oils were investigated as support materials, but the geometrical accuracy was lost since oil has a different contact angle with ice. The salt/sugar solution was identified as a support material for the ice structures. The eutectic aqueous solution of salt and glucose were investigated. It was found that the eutectic salt solution has a melting point of − 21.3 °C and glucose has a melting point of − 5.6 °C. Although salt gives a good temperature difference, it also affects the pure water ice by diffusion and melts it during support removal. Glucose was a better choice since the material removal was only 2.4% [58].

3.4 Multi-jet dispensing

Multi-jet systems use a printhead with multiple piezoelectric nozzles that jet the liquid in tandem, as per the given geometry [59]. The rasterized image is the input for the multi-jet system, unlike the g-codes in the single-jet system. The multi-jet system has benefits over the single-jet system regarding speed, accuracy and ease of operation. The 3D printed ice structures are demonstrated by the multi-jet technology [60, 61].

Multi-jet systems use printheads that are capable of depositing the liquids of the predetermined viscosity and surface tensions. The freezing subsystem is the unique feature of the SZ-AM multi-jet machine. The motion system, deposition system and the related electronics are adequately insulated to protect them from the low temperatures and the subsequent condensation of the water vapour. The workspace is enclosed in an insulated chamber to maintain the sub-zero temperatures of the part [62, 63]. The support materials are similar to the single-jet system.

4 Future scope for the research

Even though SZ-AM technologies are being explored for novel materials since 2002, they are not found commercially exploited. The following challenges of working inside a sub-zero environment are bottlenecks for the implementation of the SZ-AM on a larger scale:

- The material must remain in liquid form until it emerges out of the nozzle and shall freeze instantly on touching the substrate. This requires an appropriate heating arrangement in the deposition system.
- As aqueous materials are corrosive, the life of the deposition system will be less.
- The electronic circuitry of the deposition system shall be sealed from the condensing moisture due to low temperatures.
- The motion system uses motors, encoders, limit switches and other electrical/electronic items. These also need to be protected from damage caused by moisture.
- The temperature has to be measured at multiple locations in the chamber and controlled by the refrigeration system to maintain the desired temperature.
- The chamber shall be insulated nicely to prevent heat loss to the atmosphere.

4.1 System architecture suitable for cooling

SZ-AM process incorporates sub-zero temperatures for the phase change and maintains their solid state for the desired time. It involves an appropriate embodiment of the cooling system. SZ-AM requires variable cooling rates. High cooling rates are required initially to rapidly cool the system from room temperature to the desired working temperature. Once the working temperatures are reached, a controlled cooling rate is necessary to print the part. The cooling rate determines the quality of crystallization, strength and geometric accuracy of the part. Hence, a specialized cooling system is required.

Another challenge the cooling system poses is the condensation of the atmospheric water vapour. If the water gets condensed and frozen on the motion subsystem parts such as guide rods, ball screws and linear guides, it may affect them badly. Also, if the electronics are cooled, the water may condense on the PCBs, electrical connections and affect their working. Hence an embodiment solution for the subsystem is required to address these issues with the system architecture.

4.2 Multi-material capability

SZ-AM process has the inherent capability to work with multiple materials simultaneously. For example, as discussed in the applications, photopolymer and water are printed simultaneously, where water is used as a support material that can be readily melted. Similarly, multi-jet technology enables the deposition of multiple materials that can enhance the part's functionality and develop suitable products.

4.3 Multi-jet technology and rasterization

Multi-jet technology is faster, gives a higher resolution, and is easier to operate than the single-jet system. However, multi-jet deposition technology is different from the single jet or extrusion-based technology regarding data handling. As extrusion and single-jet processes accept g-code data, the multi-jet technique needs rasterized image data readable by the particular control system for the printhead. In single jet and extrusion-based processes, the STL file is sliced, and each slice is stored as a g-code that sends the motion data to the machine. Similarly, in the multi-jet technique, the STL file is sliced into the bitmap image, and it is rasterized into a sequence of 2-bit data for the printhead that allows the jetting to occur as per the image. Motion and the jetting are synchronized with each other using an encoder that registers the exact position of the printhead and gives feedback to the printhead controller.

Multi-jet systems are not readily available for the various liquids with a wide range of viscosity and surface tension. Hence, the solution is required to jet a wide range of liquids with various surface tension and viscosity ranges. Also, an open-source platform for the rasterization dedicated to only AM technology would be a significant breakthrough.

4.4 Application-specific challenges

As mentioned above, there are several applications of the SZ-AM process. SZ-AM machine requires a tailor-made approach to design the machine for specific applications. The materials for SZ-AM can be categorized based on their flow properties such as density, viscosity and surface tension and deposition system can be implemented.

However, for applications such as medicine, pharmaceuticals, and prosthetics, the SZ-AM machine also needs sealed chambers free from any contamination. Biocompatible materials are preferred for their construction.

It is easier for small-scale parts to construct insulation chambers; however, a spot cooling approach is suitable for large-scale parts, such as construction, etc. A constant supply of cooling gas such as liquid nitrogen/CO_2 can be given in the spot cooling approach.

5 Conclusion

- All AM processes are controlled for temperature and/or pressure. AM processes are well-established for a wide range of metals, polymers and ceramics, at ambient or higher temperatures. However, materials such as gels, aqueous solutions, colloids, slurries, etc. that are liquids at room temperature but can be solidified to make frozen objects useful for various applications. All such materials have water as a significant constituent that undergoes a phase change and maintains the object's shape.

- SZ-AM process helps in realizing the frozen objects by layered deposition of these materials in a sub-zero environment.
- SZ-AM process finds applications in a wide range of fields such as medicine, manufacturing, construction, electronic devices and pharma industries. Each of these applications is unique and significant.
- As it can be seen from the literature, the SZ-AM process inherently takes place inside an insulated chamber maintained at sub-zero temperature (typically − 20 to − 25 °C). Therefore, SZ-AM machines have to overcome architectural challenges due to low temperatures and condensation of moisture.
- SZ-AM technology primarily incorporates three modes of material deposition, viz. extrusion, single jet and multi-jet deposition, based on the viscosity of the material. For high viscosity materials, extrusion is suitable, and multi-jet deposition is the most versatile approach for low viscosity materials that enable a high resolution, speed, and ease of operation.
- Multi-jet technology is limited by the narrow range of viscosity and surface tension. If the multi-jet system is made to suit a wide range of viscosity and surface tension, newer materials can be explored for the SZ-AM process.

Funding Not applicable.

Declarations

Conflict of interest There are no conflicts of interest.

Data availability Not applicable.

Code availability Not applicable.

Ethics approval Not applicable.

Consent for publication Authors give their consent for the publication of the identifiable information.

References

1. Campbell I, Bourell D, Gibson I (2012) Additive manufacturing: rapid prototyping comes of age. Rapid Prototyp J 18(4):255–258
2. Zhang W, Leu MC, Ji Z, Yan Y (1999) Rapid freezing prototyping with water. Mater Des 20(2–3):139–145
3. Pallottino F et al (2016) Printing on food or food printing: a review. Food Bioprocess Technol 9(5):725–733
4. Tetik H et al. High Speed In-situ X-ray Imaging of 3D Freeze Printing of Aerogels, Addit Manuf 36(May): 101513, 2020.
5. Zhang HZ et al (2015) Portable, easy-to-operate, and antifouling microcapsule array chips fabricated by 3d ice printing for visual target detection. Anal Chem 87(12):6397–6402
6. Zheng F, Wang Z, Huang J, Li Z (2020) Inkjet printing-based fabrication of microscale 3D ice structures, Microsystems Nanoeng 6(1).
7. Ionescu N, Vian A, Savin A, Trifnescu M TEHNOMUS-new technologies and products in machine manufacturing technologies technical solutions to design an equipment for ice parts rapid prototyping, pp 101–106.
8. Tan Z, Parisi C, Di Silvio L, Dini D, Forte AE (2017) Cryogenic 3D printing of super soft hydrogels. Sci Rep 7(1):1–11
9. Leu MC, Garcia DA (2014) Development of freeze-form extrusion fabrication with use of sacrificial material. J Manuf Sci Eng Trans ASME 136(6):1–9
10. Huang T, Mason MS, Hilmas GE, Leu MC (2006) Freeze-form extrusion fabrication of ceramic parts. Virtual Phys Prototyp 1(2):93–100
11. Zhao D, Han A, Qiu M (2019) Ice lithography for 3D nanofabrication. Sci Bull 64(12):865–871
12. Zhang W, Leu MC Investment casting with ice patterns made by rapid freeze prototyping, pp 66–72.
13. Liu Q, Leu MC, Richards VL, Schmitt SM (2004) Dimensional accuracy and surface roughness of rapid freeze prototyping ice patterns and investment casting metal parts. Int J Adv Manuf Technol 24(7–8):485–495
14. Huang C, Leu MC, Richards VL (2004) Investment casting with ice patterns and comparison, NSF Des Manuf Grantees Conf pp 1–7.
15. Liu Q, Sui G, Leu MC (2002) Experimental study on the ice pattern fabrication for the investment casting by rapid freeze prototyping (RFP). Comput Ind 48(3):181–197
16. Richards VL et al. (2008) Rapid freeze prototyping of investment cast thin-wall metal matrix compostites I—pattern build and molding, Mater Soc Annu Meet pp 143–156.
17. Liu Q, Leu MC (1997) Study of ceramic slurries for investment casting with ice patterns, Bachelor degree thesis pp 602–611.
18. Jin J, Chen Y (2017) Highly removable water support for Stereolithography. J Manuf Process 28:541–549
19. Chen Y, Jin J SLA Additive manufacturing using frozen supports of non—sla material, US 10,894,354 B2, 2021.
20. Shakor P, Nejadi S, Paul G (2020) Investigation into the effect of delays between printed layers on the mechanical strength of inkjet 3DP mortar. Manuf Lett 23:19–22
21. . Zheng F, Huang J, Li Z (2019) Fabrication of 3D Micro Ice Structures Based on Inkjet Printing. In: Proc. IEEE Int. Conf. Micro Electro Mech. Syst., 2019-Janua, no. January, pp 368–371.
22. Hong Y et al (2018) Three-dimensional in situ electron-beam lithography using water ice. Nano Lett 18(8):5036–5041
23. Fujita H , Nakano A, Hada H (2017) Elsa: temporary ice jet 3d printing, TEI 2017—Proc. 11th Int. Conf. Tangible, Embed. Embodied Interact, pp 559–563.
24. Gannarapu A, Gozen BA (2016) Freeze-printing of liquid metal alloys for manufacturing of 3D, conductive, and flexible networks, Adv Mater Technol 1(4).
25. Adamkiewicz M, Rubinsky B (2015) Cryogenic 3D printing for tissue engineering. Cryobiology 71(3):518–521
26. Kam D et al (2019) Direct cryo writing of aerogels via 3D printing of aligned cellulose nanocrystals inspired by the plant cell wall. Colloids and Interfaces 3(2):46
27. Zhang W et al. (2019) Fabrication and characterization of porous polycaprolactone scaffold via extrusion-based cryogenic 3D printing for tissue engineering, Mater. Des., 180:107946.

28. Wang C, Zhao Q, Wang M (2017) Cryogenic 3D printing for producing hierarchical porous and rhBMP-2-loaded Ca-P/PLLA nanocomposite scaffolds for bone tissue engineering, Biofabrication, 9(2).
29. Wang C et al (2021) Cryogenic 3D printing of dual-delivery scaffolds for improved bone regeneration with enhanced vascularization. Bioact Mater 6(1):137–145
30. Lee JY, Kim GH (2020) A cryopreservable cell-laden GelMa-based scaffold fabricated using a 3D printing process supplemented with an in situ photo-crosslinking. J Ind Eng Chem 85:249–257
31. Wang Z, Florczyk SJ (2020) Freeze-FRESH: A 3D printing technique to produce biomaterial scaffolds with hierarchical porosity, Materials (Basel) 13(2).
32. Sun J, Zhou W, Yan L, Huang D, ya Lin L (2018) Extrusion-based food printing for digitalized food design and nutrition control, J Food Eng 220: 1–11
33. Zawada B, Ukpai G, Powell-Palm MJ, Rubinsky B (2018) Multi-layer cryolithography for additive manufacturing. Prog Addit Manuf 3(4):245–255
34. Dick A, Bhandari B, Prakash S (2019) 3D printing of meat. Meat Sci 153(March):35–44
35. Novedge, “Robots in Gastronomy,” 2014. [Online]. Available: https://robotsingastronomy.com/. [Accessed: 22-Oct-2021].
36. Yang F, Zhang M, Bhandari B (2017) Recent development in 3D food printing. Crit Rev Food Sci Nutr 57(14):3145–3153
37. Barnett E, Angeles J, Pasini D (2009) Robot-assisted rapid prototyping for ice structures. IEEE Int Conf Robot Autom 33(4):146–151
38. Barnett E, Angeles J, Pasini D (2009) Robot-Assisted Rapid Prototyping for Ice Structures, pp 146–151.
39. Morris M et al (2016) Mars ice house: using the physics of phase change in 3D printing a habitat with H2O. Aiaa Sp 2016(July):673–681
40. Shakor P, Nejadi S, Paul G, Sanjayan J (2019) Dimensional accuracy, flowability, wettability, and porosity in inkjet 3DP for gypsum and cement mortar materials, Autom Constr 110(December):102964, 2020.
41. Shakor P, Nejadi S, Paul G, Malek S (2019) Review of emerging additive manufacturing technologies in 3d printing of cementitious materials in the construction industry, Front Built Environ 4(January).
42. Shakor P, Nejadi S, Sutjipto S, Paul G, Gowripalan N (2020) Effects of deposition velocity in the presence/absence of E6-glass fibre on extrusion-based 3D printed mortar, Addit Manuf 32(January):101069.
43. Shakor P, Nejadi S, Paul G (2019) A study into the effect of different nozzles shapes and fibre-reinforcement in 3D printed mortar, Materials (Basel)., 12(10).
44. Gowripalan N, Shakor P, Rocker P (2021) Pressure exerted on formwork by self-compacting concrete at early ages: a review, Case Stud Constr Mater 15(July): e00642.
45. Zhang H, Li H, Wu M, Yu H, Wang W, Li Z (2014) 3D ICE printing as a fabrication technology of microfluidics with pre-sealed reagents, Proc IEEE Int Conf Micro Electro Mech Syst, pp 52–55.
46. Segura LJ, Zhao G, Zhou C, Sun H (2020) Nearest neighbor gaussian process emulation for multi-dimensional array responses in freeze nano 3d printing of energy devices. J Comput Inf Sci Eng 20(4):1–10
47. Zhang Q, Zhang F, Medarametla SP, Li H, Zhou C, Lin D (2016) 3D printing of graphene aerogels. Small 12(13):1702–1708
48. Zhang F et al (2017) 3D printing technologies for electrochemical energy storage. Nano Energy 40(August):418–431
49. Kim NP, Cho D, Zielewski M (2019) Optimization of 3D printing parameters of Screw Type Extrusion (STE) for ceramics using the Taguchi method. Ceram Int 45(2):2351–2360
50. He Q et al (2021) Additive manufacturing of dense zirconia ceramics by fused deposition modeling via screw extrusion. J Eur Ceram Soc 41(1):1033–1040
51. Guo CF, Zhang M, Bhandari B (2019) A comparative study between syringe-based and screw-based 3D food printers by computational simulation, Comput Electron Agric, 162(August 2018):397–404
52. Zhang W, Leu MC, Ji Z, Yam Y (2001) Method and apparatus for rapid freezing prototyping, US 6,253,116 B1.
53. Bryant FD, Sui G, Leu MC (2003) A study on effects of process parameters in rapid freeze prototyping. Rapid Prototyp J 9(1):19–23
54. Sui G, Leu MC (2003) Investigation of layer thickness and surface roughness in rapid freeze prototyping. J Manuf Sci Eng 125(3):556
55. Savin A, Floca A, Trifănescu M, Ionescu N, Vişan A (2015) Development of modeling process in rapid freeze prototyping. Appl Mech Mater 760:117–122
56. Sui G, Leu MC (2003) Thermal analysis of ice walls built by rapid freeze prototyping. J Manuf Sci Eng 125(4):824
57. Bryant FD, Leu MC (2009) Predictive modeling and experimental verification of temperature and concentration in rapid freeze prototyping with support material. J Manuf Sci Eng Trans ASME 131(4):0410201–0410209
58. Bryant FD, Leu MC Study on Incorporating Support Material in Rapid Freeze, pp 416–427.
59. Kamble P, Chavan S, Karunakaran KP Multi-Jet Fluid Deposition in 3D Printing : a Review, no. July, 2018.
60. Kamble PP (2021) Multimodal Freezing System for Cryogenic 3D Printing, Prepr Res Sq.
61. Kamble PP, Chavan S, Hodgir R, Gote G, Karunakaran KP (2021) Multi-jet ice 3D printing, Rapid Prototyp J, no. December.
62. Kamble P, Chavan S, Hodgir R, Gote G, Karunakaran KP Multimodal Freezing System for Cryogenic 3D Printing, Res Sq Prepr. https://doi.org/10.21203/rs.3.rs-480124/v1.
63. Liao N (2017) p3. US20170343263A1 - System and method for making an ice sculpture.pdf. United States Patent Application Publication.
64. Liu Q, Leu MC (2006) Investigation of interface agent for investment casting with ice patterns. J Manuf Sci Eng 128(2):554
65. Sijpkes P, Barnett E, Angeles J, Pasini D (2009) The architecture of phase change at McGill, Leadersh Archit. Res no. April, p 241.
66. Gupta D, Singh AK, Dravid A, Bellare J (2019) Multiscale porosity in compressible cryogenically 3D printed gels for bone tissue engineering. ACS Appl Mater Interfaces 11(22):20437–20452