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Additive Manufacturing—Review

Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials

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ABSTRACT

The rapid development of additive manufacturing and advances in shape memory materials have fueled the progress of four-dimensional (4D) printing. With the right external stimulus, the need for human interaction, sensors, and batteries will be eliminated, and by using additive manufacturing, more complex devices and parts can be produced. With the current understanding of shape memory mechanisms and with improved design for additive manufacturing, reversibility in 4D printing has recently been proven to be feasible. Conventional one-way 4D printing requires human interaction in the programming (or shape-setting) phase, but reversible 4D printing, or two-way 4D printing, will fully eliminate the need for human interference, as the programming stage is replaced with another stimulus. This allows reversible 4D printed parts to be fully dependent on external stimuli; parts can also be potentially reused after every recovery, or even used in continuous cycles—an aspect that carries industrial appeal. This paper presents a review on the mechanisms of shape memory materials that have led to 4D printing, current findings regarding 4D printing in alloys and polymers, and their respective limitations. The reversibility of shape memory materials and their feasibility to be fabricated using three-dimensional (3D) printing are summarized and critically analyzed. For reversible 4D printing, the methods of 3D printing, mechanisms used for actuation, and strategies to achieve reversibility are also highlighted. Finally, prospective future research directions in reversible 4D printing are suggested.

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1. Introduction

Three-dimensional (3D) printing, also known as additive manufacturing or rapid prototyping, has been around for three decades, ever since its commercialization in 1987 with stereolithography from 3D Systems [1]. Parts produced by 3D printing have been widely used for the prototyping of new products and the manufacturing of structures and objects that cannot be achieved via traditional manufacturing techniques. With the development of 3D printing, there are now seven process categories under the American Society for Testing and Materials (ASTM) standards [2–4]: material extrusion, material jetting, sheet lamination, binder jetting, powder bed fusion, directed energy deposition, and vat photopolymerization. The use of 3D printing is currently widespread, and 3D printing is no longer merely used for industrial or academic research purposes

[5]; rather, it is transforming from a prototyping method into a mature manufacturing method. However, 3D printing is still unable to replace most conventional manufacturing methods due to the limitations of materials, build size, and cost [6]. Instead, it complements conventional manufacturing to produce new products with increased complexity and functions. Nevertheless, the prospect of more manufacturing applications in 3D printing largely relies on the development of new materials that are suitable for 3D printing techniques.

Over the past two decades, there have been many studies on shape memory materials [7–12], which are also known as “smart” materials. These materials have the capacity to change their shape or properties under the right stimuli. Metal alloys and polymers are the most popular of these materials, and have drawn a considerable amount of attention [13,14].

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The development of 3D-printable “smart” materials has driven 3D printing to another level, known as four-dimensional (4D) printing. 4D printing is a combination of 3D printing and the fourth dimension, which is time [15–17]. This technique allows a printed object to be programmed to carry out shape change while adapting to its surroundings. This breakthrough technology is mainly fueled by the rapid development of smart materials and the latest progression of multi-material printing. Particularly due to the development of multi-material polymer printing, the 4D printing of polymers has been made possible [16], and more opportunities and applications await discovery.

The Massachusetts Institute of Technology (MIT)’s Self-Assembly Lab was among the first to develop and demonstrate the possibility of 4D printing. In his 2013 TED Talk (TED stands for technology, entertainment, and design), Skylar Tibbitts, the co-director of the MIT Self-Assembly Lab and a pioneer of 4D printing, demonstrated how 3D-printed materials can adapt to their surroundings (water, in his example) and self-assemble into different structures [18].

While 4D printing looks promising for many applications such as the packaging, medical, construction, and automotive fields, it is still a very raw and new technology with many challenges that require resolution. Significant issues include the development of shape memory materials that possess reversibility; the printability of shape memory materials, and especially reversible shape memory materials; and the repeatability of 4D printed objects.

Reversibility is usually referred to as “two-way memory” because it gives the material two permanent shapes [19]. Most current 4D printing demonstrations are one-way, which means that the devices must be reprogrammed after each recovery. Here, programming or reprogramming refers to the manual setting of a temporary shape. Adding reversibility into 4D printing will allow repetitive actuation and eliminate the need for reprogramming, which is time and labor consuming. Fig. 1 depicts the effects of irreversible (one-way) shape memory and reversible (two-way) shape memory with heating and cooling as the stimuli.

Repeatability, on the other hand, refers to the ability to repeat the entire cycle without fracture or significant change to the permanent shape. The main topics of discussion in this review are shape memory materials that can be 3D printed, their reversibility, and their repeatability.

2. 3D printing of shape memory alloys and shape memory metals

Shape memory alloys (SMAs) belong to a particular group of

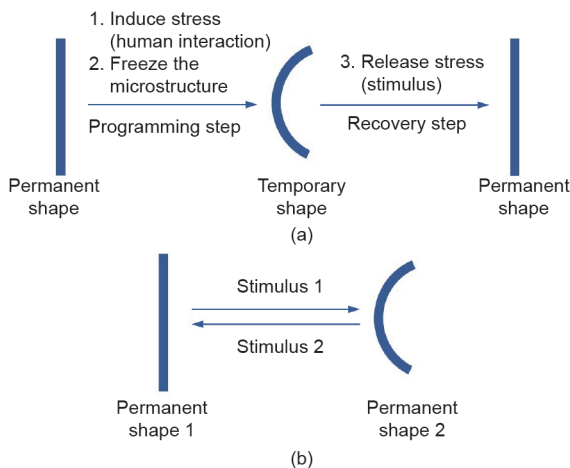


Fig. 1. (a) The process chain of an irreversible (one-way) shape memory effect; (b) the process chain of a reversible (two-way) shape memory effect.

metal alloys that are able to recover their original shape under certain stimuli. SMAs are usually subjected to a programming process between two transformation phases of metal alloys. These phases depend on differences in temperature [20] or magnetic field [21]. The transformation phenomenon is known as the shape memory effect (SME).

To achieve 3D printing of SMAs and shape memory metals (SMMs), it is necessary to understand the functioning mechanisms of different SMAs and SMMs before reviewing their repeatability and current printability.

2.1. Mechanisms of SMAs and SMMs

2.1.1. Thermal shape memory effect

First, it is necessary to know that alloys can exist in different phases and can attain different crystal structures. SMAs usually exist in two different phases with three different crystal structures (twinned martensite, detwinned martensite, and austenite), hereby giving rise to six possible transformations [22]. There are three categories of shape memory characteristics for SMAs [23,24], namely, one-way shape memory effect (OWSME), two-way shape memory effect (TWSME), and pseudoelasticity (PE) as shown in Fig. 2 [23].

In OWSME, the one-way shape memory alloy (OWSMA) retains a deformed state after the removal of an external force. When heated, it recovers its original shape. The driving force to achieve such a transformation is the difference between the chemical free energy of the phases above the austenite start temperature (A_s), which allows crystallographic reversibility [25]. At lower temperatures, the martensite structure is stable, but at higher temperatures, the austenite structure is more stable. There is a temperature range for transformation depicting the start and the end of the transformation: The start of the transformation of martensite is the martensite start temperature (M_s), and the completion of the transformation is the martensite finish temperature (M_f) [26]. SMA is usually found naturally in the twinned martensite structure. When load is applied to the SMA, it forms a detwinned martensite structure. When the SMA is unloaded, it retains the detwinned martensite structure. The start of the transformation of austenite is A_s and the completion of the transformation is the austenite finish temperature (A_f). When heated beyond A_s , the detwinned martensite structure begins to contract and transform into the austenite structure, resulting in shape recovery. If the austenite is heated beyond the temperature M_d , the highest temperature at which martensite can no longer be stress induced, the SMA will be permanently deformed [27]. Once the SMA is cooled below M_s again, the transformation will cause the austenite to revert back to the martensite structure, and the transformation will be completed below M_f .

Some SMAs obtained through a suitable thermomechanical treatment exhibit the TWSME [28], also known as reversible SME. Two-way shape memory alloy (TWSMA), unlike OWSMA, which can only remember one permanent shape, can remember shapes at both high and low temperatures. The unique functionality of this effect is that the alloy does not need to undergo external mechanical stress [29]. For TWSME, the SMA will transform between two phases, which are generally the austenite phase at high temperatures and the detwinned martensite phase at low temperatures. TWSMEs are usually achieved by tailoring a biased OWSMA actuator that behaves like a TWSMA at the structural level [30].

The last category of SME is PE. However, this effect is not as desirable as the other two forms of SME. In the mechanism of PE, the SMA reverts to its original shape completely when the load is removed between A_f and M_d , without any heat. This functionality is more like that of an elastic solid; hence, it is less important in the context of smart materials.

Hysteresis is the measure of the difference in the transition

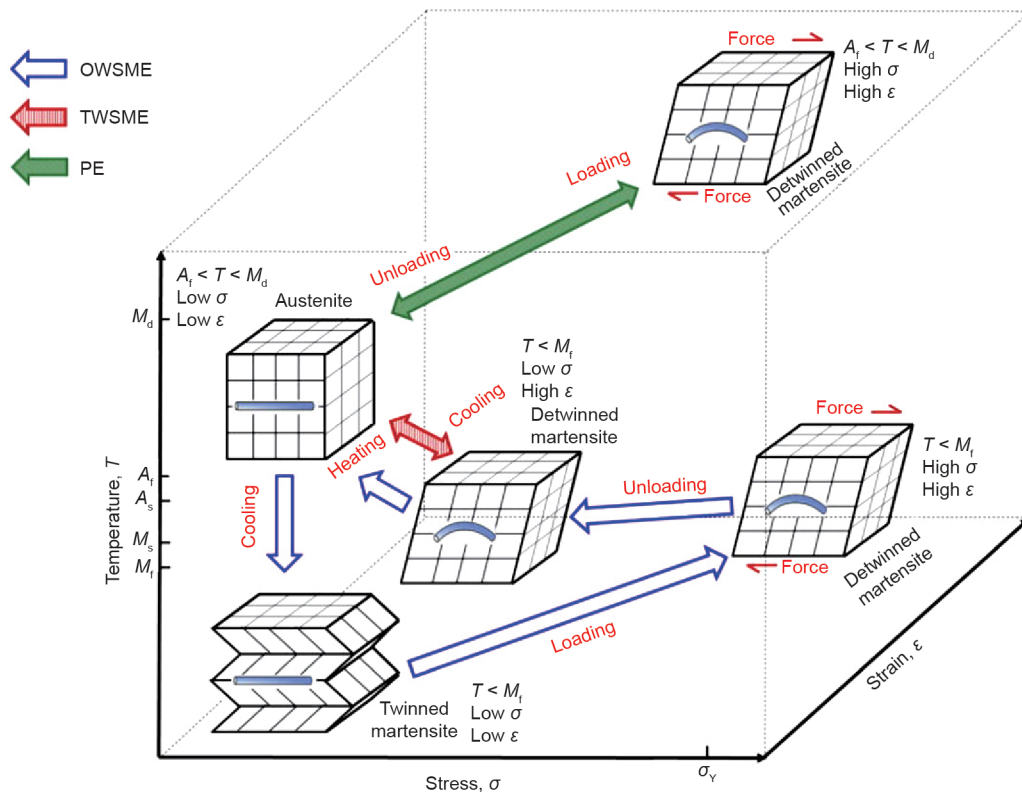


Fig. 2. SMA phases and crystal structures. When a twinned martensite is loaded till yield strength σ_y , the high stress and strain will change the martensite to detwinned martensite. After the stress is unloaded, the structure remains until it is heated to between A_i and M_d . When cooled below M_i , twinned martensite will form; if above M_i , detwinned martensite will form. (Permission obtained from Ref. [23])

temperatures between the heating and cooling of SMA. It is generally marked by the difference between the temperatures at which 50% of the material is transformed to martensite when cooled and 50% is transformed to austenite when heated [31]. For specification of applications, this is a very crucial property, as a small hysteresis is required for fast actuation application and a large hysteresis is essential for slow actuation application [32]. It is important to tailor the composition of the SMA material, the thermomechanical processing, and the working environment of the applications, as they all influence the transition temperature and the hysteresis loop. The strain levels are also important in hysteresis, as stress beyond the yield strength of martensite (approximately 8.5% for nickel-titanium alloys [33] and up to 10% for other alloys [34]) will lead to permanent deformation.

2.1.2. Magnetic shape memory effect

Magnetic SMAs are also known as ferromagnetic SMAs. The mechanisms used for magnetic SMAs are twin boundary motion [35], also known as magnetoplasticity or magnetically induced reorientation (MIR), and magnetic-field-induced phase transformation.

The twin boundary motion of the martensitic structure depends on the difference in magnetic energy, which exceeds the mechanical energy required for the displacement of atoms near the twin boundary. The difference in the magnetic energy is due to the various orientations of magnetic moments in twin-related variants. This MIR will result in a sudden increase in the magnetization and lead to shape change [36,37]. The increase in magnetization allows the actuation frequency to be higher because the actuation energy is transmitted by a magnetic field, which is much faster than a heat-transfer mechanism [38]. However, ferromagnetization is lost at high temperature, suggesting that magnetic SMA can only function at low temperatures [23].

The second mechanism is magnetic-field-induced phase transformation. This mechanism is similar to the temperature-induced martensitic transformation mentioned earlier in the discussion on the thermal SME. In addition to the directional energy induced by the magnetic moments, the Zeeman energy (ZE) plays a crucial role in this mechanism [39]. The ZE is the potential energy of a magnetized body in an external magnetic field, otherwise known as the external field energy. The ZE comes from the difference in the saturation magnetizations of phase transformation, and it increases continuously with the magnetic field. However, ZE only vaguely depends on crystal orientation, meaning that polycrystals can also be utilized as actuators. The ZE can be maximized by transforming between different phases such as from the ferromagnetic phase to the paramagnetic or antiferromagnetic phase, or vice versa, as the difference between saturation magnetizations is much larger.

2.2. Examples of 3D printing of SMAs and SMMs

The development of 3D-printed SMAs can yield structural materials that can be used on a larger scale than polymers, for applications such as construction and medical devices [16]. New perspectives on shape memory application will be opened up in this way, as 3D printing methods can be used for complex geometries that are impossible to realize by any other means. Dental braces are one example of how the 4D printing of metals may be applicable. At present, nitinol (nickel titanium, NiTi) wires are used for teeth correction. NiTi is also used in self-expanding stents [40]. When using 4D-printed stents, the stents can be customized for the patient and can be activated without the balloon process, thus reducing the invasiveness of the surgery. Such SMAs have yet to maximize their potential, as most conventionally produced SMAs are bounded by simple geometry [41]. In the 3D printing of metals, minimal distortion due to stress build-up is usually desirable; however, the aim of the 4D

printing of metals is to induce programmability for transformation into another shape. The actuation is due to the application required.

NiTi is one of the most popular and widely researched SMAs. Although NiTi alloys have many outstanding functional properties and exhibit the best shape memory behaviors, such as the high percentage of shape recovery of 8%, they are not easy to fabricate by conventional methods [41]. There are three main reasons for this difficulty. First, regarding the mechanism of NiTi alloys, a change in composition can affect the transition temperature. Impurity elements can be picked up during high-temperature processing, resulting in oxidation and microstructural defects [41]. Second, the shape memory properties of NiTi alloys make it difficult for precise machining and result in a substantial amount of tool wear [42]. Third and finally, shape-setting and heat treatments such as annealing can affect the phase transformation behavior of a NiTi alloy [43].

2.2.1. Selective laser melting

Additive manufacturing is a possible solution for the fabrication of NiTi parts [44]. Selective laser melting (SLM) is an additive manufacturing process that was researched for this purpose [45]; it was shown to reduce the number of manufacturing cycles, as minimal machining and thermomechanical treatment are needed. SLM also allows an alloy to have a higher micro-hardness, as reported by Shishkovsky et al. [46].

However, there are some problems presented by SLM nitinol parts. Nitinol produced by SLM has a lower content of Ni due to evaporation because Ni has a lower evaporation temperature than Ti, causing it to have a higher tendency to evaporate [47–49]. A decrease in Ni content was found to lead to an increase in the phase-transformation temperature [50]. A decrease in Ni content can also be contributed by the formation of Ni-rich NiTi alloy [42,51,52].

A surprising observation regarding nitinol produced by SLM is that it resolves the issue of an increase in the impurity level in conventional methods. There was no increase in impurities in the NiTi alloy produced by SLM [47]. This result might be due to the inert gas in the chamber preventing impurities from forming. The NiTi alloys produced were tested through deformation followed by heat recovery, and were found to return to their original shape.

In a compression test carried out by Meier et al. [53] to study the mechanical and functional properties of SLM NiTi parts, the researchers observed that SLM NiTi parts have lower fracture strains and stresses than conventionally made NiTi parts. However, SLM NiTi parts do exhibit higher reversible strains and lower irreversible strains than conventionally made NiTi parts. It is important to note that the tests were all performed under compression stress. Andani et al. [54] also conducted further testing on the elastic modulus and ductility of SLM-fabricated NiTi SMA, and found that these features are largely dependent on porosity and pore structure. Further studies have to be carried out under tensile stress in order to obtain a more thorough understanding of the functionality of SLM NiTi alloys.

Besides NiTi alloys, research in the additive manufacturing of other types of SMAs has also been explored. One example is the fabrication of Cu-Al-Ni-Mn SMA using SLM [55].

2.2.2. Electron beam melting

Due to the strain recovery effect displayed by NiTi alloys, Elahinia et al. [41] saw the possibility of 3D-printed NiTi parts in biomedical applications; to be specific, nitinol has a very similar stress-strain curve to that of the widely used stainless steel. These researchers manufactured a porous NiTi implant using electron beam melting (EBM) [41]. The benefits of both shape memory and customization were maximized using a 4D printing technique [56]. The SME provides two benefits in this case: enhanced bone fixation and minimi-

zation of invasive surgery [57]. In a recent study, Le et al. [58] managed to 3D print an SMA penile prosthesis prototype.

2.2.3. Laser metal deposition

Another technique used to print SMA is laser metal deposition (LMD). Khademzadeh et al. [59] studied the parameters and possibility of single-phase NiTi production by means of micro LMD. LMD was also used to fabricate copper (Cu) alloys [60].

2.2.4. Processing characteristics

In a properties study by Haberland et al. [42], experiments were carried out on SLM NiTi samples that were produced under an argon atmosphere with a Realizer SLM 100 (Realizer GmbH, Germany) commercial SLM workstation. The printed layer thickness was 50 μm and the laser density was 85 $\text{J}\cdot\text{mm}^{-3}$. Heat treatments were performed in a muffled furnace under constant argon flow and the solution annealing conditions were 1225 K for 5.5 h, under H_2O . Heat treatment will affect the step transformation and the properties after the cyclic loading. Solution annealing decreases the phase temperature slightly, though it is still higher than the transformation temperature of the initial powder. While results have shown that an aging treatment will lead to a higher transformation temperature due to loss of Ni, the behavior of a mildly aged SLM NiTi material (725 K, 24 h) is the most comparable to that of conventionally produced NiTi material. Irreversible strain accumulation is due to the formation of dislocations. The formation of Ni-rich precipitates during the aging process acts as a resistance to dislocations. However, coarse precipitates lose the potential to support martensitic transformation [61]. Thus, SLM material treated with an even milder aging (625 K, 24 h) is highly reversible, with less irreversible strain being accumulated.

Another study was carried out by Dadbakhsh et al. [62] to examine how the parameters of SLM will influence the geometrical characteristics, shape memory response, and mechanical behavior. In this study, SLM samples were produced with two scanning parameters: high laser power adjusted to a high scanning speed (HP), and low laser power adjusted to a low scanning speed (LP). It was observed that the struts produced with HP were thicker with higher volume fraction, whereas those produced with LP had volume fractions that were more comparable to the design fractions, especially when the struts were over 250 μm . Lower transformation temperature is required for HP samples as compared to LP samples. This is due to the high cooling rate, which restricts precipitation and grain size, thereby stabilizing the austenite subgrains. Regarding compression behavior, HP samples were found to withstand a higher load. This could be due to the higher volume fraction, although HP samples are still stronger at comparable actual fractions.

2.3. Repeatability

One of the issues limiting the application of SMA is functional fatigue during repeated actuation through repeated mechanical or thermal loading. The increased accumulation of irrecoverable strain determines the functionality, durability, and service life of SMA [63–65]. Defect generation and transformation cycling are positively proportional, as dislocations, grain refinement, and the formation of special grain boundaries (Σ boundaries) occur during transformation cycling [66,67]. In a review, Bowers et al. [66] suggested that other than the normal martensitic phase-transformation pathway, an additional pathway is activated during phase-transformation cycling. This additional pathway is known as the symmetry-dictated non-phase-transformation pathway (SDNPTP), and may play a key role in functional fatigue. They also proposed several strategies to suppress SDNPTP in order to improve the fatigue resistance of SMAs.

Cyclic experiments were carried out by Haberland et al. [42] on

the degradation of SME. In the first cycle, the SLM material displays a broad hysteresis with a significant plateau; irreversible strain accumulates in each cycle, and the hysteresis width decreases accordingly. However, the SLM sample exhibits higher reversible strain in the first cycle than a conventional NiTi sample. This suggests that an SMA made of an SLM-formed material is likely to have a higher repeatability than a conventional SMA.

2.4. Reversibility

As mentioned in the discussion on mechanisms, there is an effect known as TWSME in metals. After undergoing certain heat treatments [68], OWSMAs are able to exhibit TWSME. One such method is thermomechanical training after heat treatment [69]. Wang et al. [69] introduced TWSME to a narrow hysteresis TiNiCu SMA. Afterwards, the spring was able to contract when cooled and extend when heated, and the recovery rate of the spring increased to 58%. Another method that can induce TWSME in an alloy is electrochemical hydrogenation [70]. However, in that case, the variation of the TWSME was very small during the first 50 cycles.

TWSMAs are rarely applied commercially due to tedious training requirements. In addition, they usually produce about half of the recovery strain provided by OWSMAs for the same material, and the strain tends to deteriorate quickly, especially at high temperatures. The main issue with TWSMAs is that the maximum strain and deformation is only 7% [28].

As of now, no reversible 4D-printed SMAs have been made, due to unresolved issues in 4D printing such as low recovery strain, lower Ni content due to evaporation (as most metal additive manufacturing requires high energy), and poor surface finish [71].

3. 3D printing of shape memory polymers

Compared to SMAs, shape memory polymers (SMPs) have more advantages. They have a higher recoverable strain of up to 400%, compared with 8%–12% for SMA. They also possess more tunable properties that may be achieved through adjusting molecular weights and by forming composites [72]; some of the latter are biocompatible and biodegradable, and are therefore suitable for biomedical devices. Lastly, SMPs are lightweight [73], and can hence be used in automotive, aerospace, and other such applications [74–79].

3.1. Mechanisms of SMPs

SMPs consist of netpoints and molecular switches that are either physical or chemical crosslinks. These crosslinks contribute to the thermal transition as switching domains. For thermoplastics, the formation of phase-segregated morphology is the fundamental mechanism behind the SME of the material. One phase functions as the molecular switch and the other provides the physical crosslinks. For thermosets, the switch segments of chemical crosslinks are the network chains between netpoints, and the thermal transition of polymer segments is used as the shape memory switch. In comparison with thermoplastics, thermosets usually display less creep; on the other hand, there is less irreversible deformation during recovery. In addition, thermosets usually display better chemical, thermal, mechanical, and shape memory properties than thermoplastics [80].

Although there are many possible stimulus types, this paper only discusses the three most common types of stimuli for SMPs: temperature variation (thermo-responsive), chemical (chemo-responsive, inclusive of water and pH changes), and light (photo-responsive without temperature variation) [81].

There are several working mechanisms to achieve SME in polymers.

3.1.1. Thermo-responsive SMPs

SME induced by heat in polymeric materials is based on a dual-component system in which one component (usually the matrix) remains elastic throughout and the other component (the fibers) can reversibly change in stiffness depending on the temperature range, which is the reversible switch [82]. The glass transition temperature and melting temperature are commonly used to achieve a change in polymer stiffness for thermo-responsive SME.

There are two stages in a typical SME cycle: the programming process, in which the material is deformed into a temporary shape, and the recovery process, in which the shape is recovered [83]. Utilizing these basic two stages, there are three working mechanisms for thermo-responsive SMPs: dual-state mechanism (DSM), dual-component mechanism (DCM), and partial-transition mechanism (PTM), as shown in Fig. 3 [84].

(1) **Dual-state mechanism.** The glass transition state is generally used in the DSM [85]. Above the glass transition temperature (T_g), polymers are in a rubbery state; for example, elastomers generally have a T_g that is lower than room temperature and, therefore, they are rubbery at room temperature [84]. As such, they are more flexible and can be deformed easily. Below T_g , the polymer is in the glassy state, and is more brittle and hard. When the distorted shape is maintained while cooling to below T_g , the micro-Brownian motion is frozen in the glassy state. The distorted shape is largely retained even when the applied constraint is removed. The polymer returns to its rubbery state only upon being heated to above T_g , which reactivates the micro-Brownian motion and results in shape recovery [86].

Since glass transition is a commonly observed phenomenon in most polymers, thermo-responsive SME may be an intrinsic property of almost all polymers and their composites. Crosslinks, whether physical or chemical, are required to store the elastic energy, which provides the driving force for recovery [87].

(2) **Dual-component mechanism.** The DCM usually has two or more components, which can have a hard/soft segment structure,

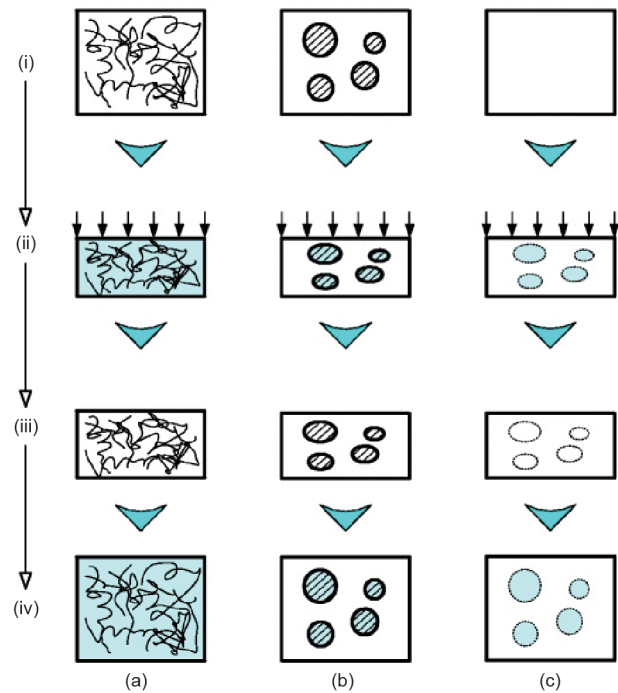


Fig. 3. Basic working mechanisms for thermo-responsive SMPs. (a) DSM; (b) DCM; (c) PTM. Four steps: (i) original sample at low temperature; (ii) upon heating and compressing; (iii) after cooling and constraint removal; (iv) after heating for shape recovery. (Permission obtained from Ref. [84])

or an elastic matrix/transition inclusion [88]. The hard segment or elastic matrix is relatively elastic throughout so that it can store elastic energy during programming. The soft segment or transition inclusion is considered to be the transition component, with a stiffness that changes upon heating. The transition component prevents shape recovery at low temperatures due to higher stiffness at low temperatures. Reheating the component softens the transition component to remove the constraints, and the stored elastic energy is activated to return the polymer back to its original shape [82].

(3) **Partial-transition mechanism.** In the PTM, rather than heating the polymer to above T_m (melting temperature) or T_g (glass transition temperature) as in the DSM or DCM, the polymer is heated to a temperature that lies within the transition range. In this case, the unsoftened portion serves as the elastic component to store elastic energy, and the softened portion behaves as the transition component [84].

In practice, DSM, DCM, and PTM can be used individually or in combination.

Even though it is an unconventional method, cooling can be used to achieve shape memory. It functions in an opposite way to heating. For example, cooling was applied to a hybrid made of polymeric sponge filled with an aqueous solution of Pluronic 407 [89]. Most thermos-responsive SMPs are heated past T_g ; next, stress is induced to allow shape change, followed by cooling to fix the temporary shape and then heating to achieve shape recovery. In the method suggested by Wang et al. [89], the radial sponge is cooled before applying stress and heating to 35 °C to achieve temporal shape fixation. It is interesting to note that shape recovery can be attained via cooling or soaking in water.

3.1.2. Chemo-responsive SMPs

The plasticizing effect is widely observed in polymers upon immersion into an appropriate chemical [90]. The plasticizing effect reduces the T_g of the polymer; therefore, it may not be necessary to heat over T_g in order to trigger a transition. This effect provides an alternative for shape recovery. Chemo-responsiveness can be triggered by the pH value, ionic strength, or quality of the agent [91].

There are three mechanisms for chemo-responsive SME: softening, swelling, and dissolving. For chemo-responsive SME, gels and hydrogels have been widely used to achieve shape memory [12].

(1) **Softening.** A study by Huang et al. [92] showed that actuation in polyurethane (PU) can be achieved through moisture or water as a stimulus. When a piece of pre-bent PU wire with an initial T_g of 35 °C was immersed in room-temperature water at 22 °C, it softened and gradually returned to its original shape. No swelling occurred, as the absorbed water was less than 5%. Ethanol was also shown to act as a stimulus to PU, at a much faster rate.

(2) **Swelling.** A piece of pre-deformed polystyrene can recover its original shape upon immersion in room-temperature acetone for 16 h [84]. Similarly, although a soft contact lens is glassy without water, it becomes soft and rubbery after being soaked in water or solution, suggesting a decrease in T_g .

Another type of SMP that swells is shape-changing gel (SCG), which is a hydrogel. The swelling is affected by changing the degree of crosslinking or by inducing change in the miscibility of polymeric segments and solvent molecules [91]. For example, increasing the degree of crosslinking can be achieved by adjusting the pH value, and an increase in crosslinking density will reduce the amount of swelling.

In a study done by Varghese et al. [93], the hydrogel reversibly transformed from a cylindrical gel sample into a hollow spherical or ellipsoidal shape upon manipulation of the presence of metal ions such as Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , or Fe^{3+} . The hydrogel regained its initial shape after the metal ions were washed out using a hydrogen chloride solution. In this case, the concentration of the metal ions acted

as the stimulus for chemo-responsive shape change.

(3) **Dissolving.** When softening is taken to the extreme, the transition component will be removed by dissolving into the surrounding medium [94]. An original star-shaped ring made of silicone filled with 70 vol% of sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) was first expanded by heating to the melting point of sodium acetate trihydrate, and then cooled to room temperature (around 22 °C) in water. The sodium acetate trihydrate gradually dissolved into the water, allowing the silicone to recover its original star shape.

3.1.3. Photo-responsive SMPs

Lendlein et al. [78] reported that polymers containing cinnamic groups are able to form new temporary shapes when exposed to ultraviolet (UV) light illumination. These shapes are stable for an extended period, but they can recover their original shape at ambient temperature when exposed to UV light of a different wavelength. In a test (Fig. 4) [78], photo-responsive SMPs, like thermo-responsive SMPs, were found to require programming via an external force in order to induce a deformation in the polymer. A free-standing non-deformed polymer was also tested, but did not yield the same result. Lendlein et al. [78] managed to obtain nearly the original length after shape recovery, and two cycles were carried out. No change was observed in the shape memory properties; however, the film changed from clear to pale yellow. It is likely that partial cleavage of the photo-reversible crosslinks may lead to changes in the mechanical properties. This work established a foundation for many other researchers who subsequently worked with photo-responsive SMPs, particularly in the aspects of micellular work and hydrogels [95–98].

3.2. Examples of 3D printing of SMPs

Two main types of materials produced by additive manufacturing are used to realize 4D printing: SMPs, which are capable of temporal shape fixation and which recover upon heating; and gels, which swell when solvent molecules diffuse into the network.

3.2.1. Polymer jetting by PolyJet

One of the first types of 4D printing has a chemo-responsive—and particularly water-activated—mechanism. In collaboration with Autodesk, Inc. and Stratasys, Ltd., Tibbits [16] researched the 3D

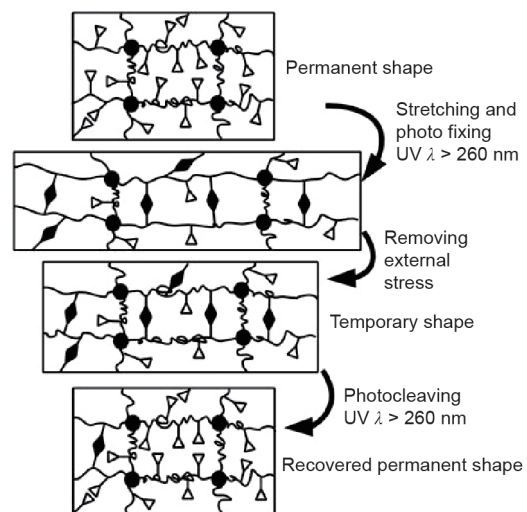


Fig. 4. Molecular mechanism of a photo-responsive SMP in a grafted polymer network. Hollow triangles represent chromophores, filled circles represent permanent crosslinks, and filled diamonds represent photo-reversible crosslinks. (Permission obtained from Ref. [78])

printing of smart materials that expand when exposed to moisture. The researchers started with a one-dimensional (1D) strand that self-assembled into the two-dimensional (2D) word “MIT.” They then proceeded with 2D plates that folded into a 3D cube (Fig. 5) [16]. The material used was a hydrophilic polymer that swells in water and expands up to 150%. In this case, the researchers used a rigid material as the framework and programmed the smart material to act as a hinge for the object. Only the smart material section (the hinge) actuated when the object was submerged in water.

A more common activation method for 4D printing utilizes high temperature to trigger shape change by combining heat and stress [99]. The shape memory composite can bend at different rates and in different directions, depending on the design of the hinges. Ge et al. [99] created a printed active composite (PAC), which was printed using a 3D multi-material polymer printer (Objet260 Connex, Stratasys, Ltd., USA). A PAC is a bilayer composite system comprised of SMP fibers that are covered by the matrix. The matrix is an elastomer so that after the stress is released, it returns to the stress-free state. However, the SMP retains the stretch configuration, as the microstates of the molecules are frozen. When the PAC is heated beyond T_g again, the original shape is recovered. This cycle is displayed in Fig. 6, which portrays earlier research by Ge et al. [99] in which they studied the bending of the PAC laminates by aligning the SMP fibers differently, thus forming coils, twists, and waves. This study laid the foundation for their subsequent studies in making the PAC functional. As noted earlier, Ge et al. [100] simulated the folding of a cube and a pyramid with PACs as the hinges. In a similar study, the mechanism of the shape change and a theoretical model were proposed and experimented on in order to understand the complex material behavior [101].

This concept of PAC bending during recovery has been improved in order to achieve sequential shape change and multi-shape change [102–104]. The percentage of fibers to matrix was varied to achieve sequential shape change with the same materials [103,104].



Fig. 5. Folding of an unpacked cube with hinges composed of a smart hydrophilic polymeric material; when submerged in water, the smart material actuates and the object folds into a cube. (Permission obtained from Ref. [16])

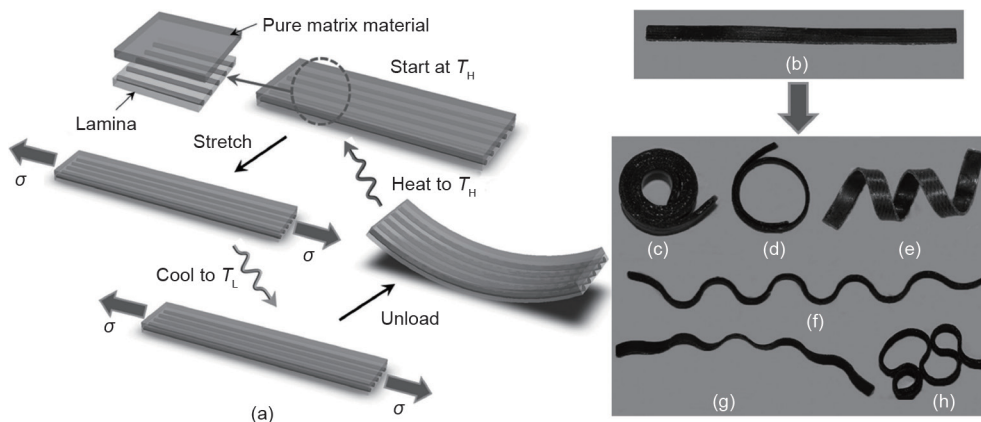


Fig. 6. Complex low-temperature shapes of PAC laminates obtained by design of the laminate architecture. (a) A bilayer laminate (with one layer designed as a lamina with fibers at a prescribed orientation and the other layer as a pure matrix material) is printed, and then heated to T_H (high temperature of 60 °C), stretched, cooled to T_L (low temperature of 15 °C), and released. Upon release of the stress, it assumes a complex shape, depending on the laminate architecture. Upon reheating, it then assumes its original shape, a flat rectangular strip. (b) An actual strip in its original shape. (c)–(h) Results of this process with differing fiber architectures. (Permission obtained from Ref. [99])

In earlier works in SMPs, researchers achieved a tri-SME by using multiple materials with two or more transition points [105–111]. To parallel the work of conventional manufacturing with 4D printing techniques, Wu et al. [102] demonstrated an approach to design and manufacture a flat layered composite with a myriad of digital SMP fibers in the matrix. The parameters to achieve controlled bending and shape change were also studied and optimized in order to achieve different desired temporary and permanent shapes. The possibility for shape variability was demonstrated further by extending this concept to obtain an orchid shape [112]. Morphing of the structure was achieved by creating different digital materials by varying the T_g while using only two base materials.

3.2.2. Stereolithography

The limitation of the PAC method described above is that the materials offered by Stratasys, Ltd. are proprietary, and therefore cannot be manipulated. A new 4D printing method proposed by Ge et al. [113] uses high-resolution projection microstereolithography (PμSL). The main advantages of this method are the resolution and the freedom to tune the material properties. Shape memory was attained with a single material SMP with a T_g of 43 °C [113]. A similar study was reported by Choong et al. [114], who also proposed several applications, such as stents that can be reduced to a smaller diameter for minimally invasive surgery, and a microgripper. In another study, conductive carbon nanotube ink was printed onto a stereolithography-printed polycaprolactone (PCL) model that was intended to function as a shape-memory-based electronic device [115]. Two other applications proposed by Zarek et al. [116] for 4D printing using digital light processing (DLP) printing were dynamic jewelry and fashionwear.

Miao et al. [117] 4D printed a novel renewable soybean oil epoxidized acrylate using stereolithography-based bioprinting. “4D bioprinting” refers to groups of human-made programmable self-assembling, self-folding, or self-accommodating technologies that are triggered by the external environment [118]. The scaffold displayed SMEs, with a temporary shape that was fixed at -18 °C and an initial shape that was fully recovered at human body temperature (37 °C). This result indicates great potential for biomedical application. In addition, cytotoxicity testing has statistically proven that the adhesion and proliferation of multipotent human bone marrow mesenchymal stem cells (hMSCs) are comparable to those of polylactic acid (PLA) and PCL.

3.2.3. Fused deposition modeling

Another 3D printing technique that allows shape memory or

shape shifting via a heating mechanism is fused deposition modeling (FDM) [119]. In this particular case, the material used was PLA. Internal stress accumulates in the printed material, as heating and rapid cooling cycles occur during the fabrication process due to constraints of the platform or existing layers. After the completion of the printing, the internal stress is stored in the printed material for a long time, until the material is heated beyond T_g .

The printing of a biocomposite via FDM provided an example of advancement in 4D bioprinting [120]. The printed wood-reinforced biocomposite displayed poorer mechanical properties than conventionally produced wood biocomposites. However, the wood biocomposite in this study was found to be unlike other conventional wood-reinforced biocomposites, for which the goal is to increase strength and stiffness; rather, the novel functionality of this composite was the achievement of self-shaping actuation. The use of FDM led to a large increase in water intake, similar to the behavior of polyhydroxyalkanoate (PHA) or PLA, thus allowing swelling as a stimulus [121]. The use of natural biopolymers may better suit applications in the biomedical field.

3.2.4. Hydrogel extrusion

Researchers at the School of Engineering and Applied Sciences (SEAS) in Harvard University created a 4D printing system that was inspired by biomimetic 4D printing in order to simulate how a botanical system responds to external stimulus [122]. They developed a hydrogel composite that can be 4D printed via extrusion into a programmable bilayer architecture. The hydrogel swelling is anisotropic in order to control the intricate shape changes that occur upon hydration [123,124]. The print path was also manipulated in order to achieve different bending and twisting conformations. The researchers managed to simulate the shapes of an orchid and a calla lily flower.

All of the work described above was only able to achieve single-direction shape memory. After every use, the composite requires reprogramming. Therefore, the functionality and application of these composites are for more complex structures that do not require reversible shape changing, or that only require a single shape change, such as a cardiac stent [125].

3.3. Reversibility

As mentioned earlier, advancement in materials is a huge driving force for advancement in 3D printing. Similarly, the recent advancement in reversible SMPs has driven more studies in reversible 4D printing. Reversibility in SMPs promotes more functional usage in all industries, as it reduces the effort of constant reprogramming. This is particularly useful for biomedical applications where, for example, implanted devices cannot be reprogrammed manually, and reversibility using external conditions will be needed [126].

Most one-way SMP composites that use heat as the recovery mechanism undergo programming to attain a temporary shape. The programming step is usually manual stress [5,16,18,100,103,112,113,125]. To achieve a TWSME, the programming step must be removed or be inbuilt into the SMP composite in another way during manufacturing. Potential two-way shape memory properties were found in liquid crystal elastomers (LCEs); however, these have limited industrial application due to their high manufacturing cost and unstable SME [127]. Therefore, a laminate of SMP with PU was introduced to achieve such an effect [128]. When it is heated to 60 °C, the laminate curls; when it is cooled to room temperature, it uncurls. After the training cycle, this was shown to achieve good repeatability. Many other subsequent studies into polymer laminates have shown similar promising results [129,130]. Similarly, other research has employed different mechanisms to achieve reversible SMP [131]. These works indicate the huge possibility for reversible 4D printing.

As noted earlier, most 4D printing techniques are not reversible,

and must be programmed, by inducing human interactive stress, and then stimulated by external conditions to recover. To enhance the functionality of 3D-printed SMPs, reversibility is essential. Although reversibility is not very common, there have been several breakthroughs in attaining reversible SMPs.

3.3.1. Reversibility achieved by polymer jetting by PolyJet

The first of these breakthroughs was a study conducted by Mao et al. [132]. Instead of having one stimulus, these researchers incorporated a design with two stimuli by incorporating both SMP and hydrogels. The SMP is stimulated by temperature, while the hydrogel swells in the presence of an aqueous solution. Having two mechanisms allows switching between two stable configurations. The two key concepts in this design are to have the hydrogel's swelling force be the force to induce internal stress to the SMP, and to have the temperature sensitivity of the SMP properties regulate the time for shape changing. An additional layer of hydrogel between the standard SMP and the elastomer bilayer allows the PAC to shift from one-way actuation to two-way actuation. There are five stages in the cycle. First, the component is soaked in cold water for 12 h. Next, it is placed in hot water to allow the SMP to be heated past T_g in order to allow bending. The component is then cooled to room temperature, and left to dry. The hydrogel shrinks during drying. Lastly, to achieve recovery, the component is heated again.

3.3.2. Reversibility achieved by hydrogel extrusion

Another recent study by Naficy et al. [133] achieved reversibility by having two different stimuli: hydration and temperature (Fig. 7). Reversibility was achieved using a 3D-printed hydrogel-based ink. The flat structure of a cube was printed with hydrogel using an extrusion printer, and the hinges were made from various hydrogel ink formulations. The researchers used a cube model to optimize the parameters and predict the bending characteristics. Producing the whole structure in hydrogel enhances the suitability of its application in biomedical engineering, as it can be used to mimic the complex movements of native tissues [134].

4. Summary

The additive manufacturing techniques and applicable shape

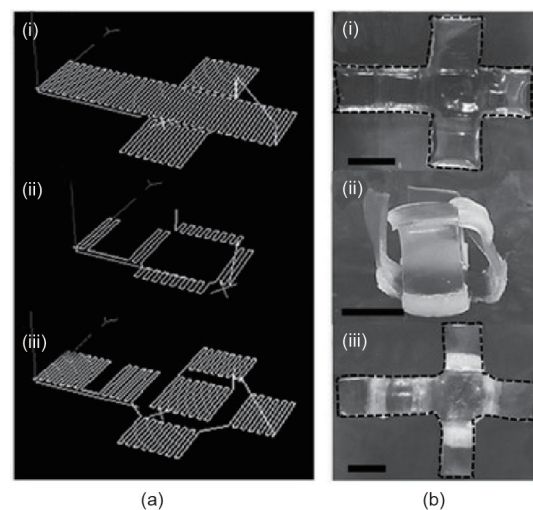


Fig. 7. The printing pattern used for a cubic box, and the resulting print at various temperatures. (a) Patterns for the print head movement to construct: (i) the base; (ii) the actuating parts; (iii) their surrounding matrix. (b) A series of images of the printed box: (i) the box as printed; (ii) the same printed box in a swollen state at room temperature; (iii) its thermal response at 60 °C. The scale bar is 1 cm. The broken lines highlight the edge of the hydrogels. (Permission obtained from Ref. [133])

memory materials for each technique are summarized in Table 1 [4,16,41,44–60,99–111,113–117,119–121,123–125,132–134].

5. Conclusions and the future of reversible 4D printing

Compared with SMAs, SMPs have a brighter future and have shown faster development in additive manufacturing, due to more stimuli and a greater variety of materials. Although SMPs have been around for three or four decades, as shown in Fig. 8 [13,14,16,102,109,127,132,133,135–142], the development of the multi-SMP took almost two decades, and it took another two years for the development of the first reversible SMP. However, the progress from the 3D printing of one-way SMPs, to multi-shape SMPs, and then to the most recent achievement of reversible 4D printing occurred over a mere three years. The development of smart materials has established a foundation for a faster pace in the development and improvement of 4D printing.

Table 2 consolidates all the different stimuli that may be used to activate SMAs and SMPs, whether constructed via conventional fabrication or 3D printing. This table indicates that more mechanisms are used in conventionally fabricated shape memory materials than in 4D printing. This is due to the limitations of available techniques in 3D printing, and to a lack in the variety of materials that are usable in 3D printing. The number of materials and techniques available for 3D printing directly relate to the available mechanisms for 4D printing. Similarly, although reversibility is not impossible in 4D printing, the design of reversibility requires a thorough understanding of SMEs and of the limitations set by the current printing methods and mechanisms of material activation.

The development of polymers for 4D printing has moved from single-stage recovery to multistage recovery. In multistage recovery, the stage is controlled by manipulating the same stimulus, which is mostly performed via precise temperature control [102,103]. As the relevant techniques and control mature, the feasibility of reversible

Table 1
Summary of additive manufacturing techniques and applicable shape memory materials for each technique.

AM process categories based on ASTM F2792 standard [4]	AM systems	Applicable materials	Refs.
Binder jetting	NA	NA	NA
Directed energy deposition	LMD	Metals	[59,60]
Material extrusion	FDM	NiTi and Cu alloys	[119–121]
	Hydrogel extrusion	Polymers PLA and wood-reinforced composites	[123–125,133,134]
Material jetting	Material jetting by PolyJet	Polymers	[16,99–111,132]
		Proprietary materials	
Powder bed fusion	SLM	Metals	[44–55]
	EBM	Metals NiTi and Cu-Al-Ni-Mn alloys	[41,56–58]
Sheet lamination	NA	NA	NA
Vat photopolymerization	Stereolithography	Polymers	[113–115,117]
		PCL and novel renewable soybean oil epoxidized acrylate	
	DLP	Polymers Methacrylate PCL	[116]

AM stands for additive manufacturing.

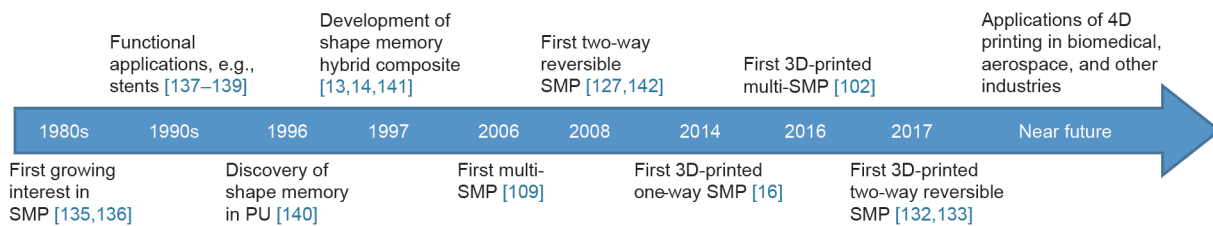


Fig. 8. Timeline of the progress in SMPs and 3D-printed SMPs.

Table 2
Summary of the available stimuli for conventional SMAs, 3D-printed SMAs, conventional SMPs, and 3D-printed SMPs.

	Conventional SMAs	3D-printed SMAs	Conventional SMPs	3D-printed SMPs
One-way	<ul style="list-style-type: none"> • Thermo-responsive • Magnetic-responsive 	<ul style="list-style-type: none"> • Thermo-responsive 	<ul style="list-style-type: none"> • Thermo-responsive • Chemo-responsive • Photo-responsive • Mechano-responsive and more 	<ul style="list-style-type: none"> • Thermo-responsive • Chemo-responsive • Photo-responsive
Two-way/reversible	<ul style="list-style-type: none"> • Thermo-responsive 	–	<ul style="list-style-type: none"> • Thermo-responsive in LCE • Thermo- and mechano-responsive in semi-crystalline elastomer laminates 	<ul style="list-style-type: none"> • Thermo- and chemo-responsive

4D printing has been tested and achieved. The research conducted by Mao et al. [132] and Naficy et al. [133] are very similar to research that was conducted on reversible SMPs fabricated by conventional methods, in which researchers designed components to induce internal stress via a different stimulus in order to allow transformation to a second permanent shape. These two studies used the same mechanisms with different materials and applications in mind. The two mechanisms are chemo-responsiveness and thermo-responsiveness. With this progress, more studies can be steered in the direction of combining two or more stimuli to achieve reversibility in 4D printing, and more functional purposes will be available for daily application. With a number of mechanisms that are possible for SMP, many combinations of stimuli are likely and will serve different purposes; examples include a sun shade that activates itself according to the amount of sunlight [143], switches that activate themselves according to the external environment, and many more. SMPs can also be used in biomedical applications that require reversible actuation. The prospects and importance of 3D printing can be expanded with the growth of reversible 4D printing.

However, limited reversibility has been achieved for the 4D printing of metals. This is because even via conventional fabrication, tedious training is required and there is poor fatigue resistance, leading to quick loss of reversible strain. In addition, there are other limitations and challenges that need to be overcome even for OWSMAs, before researchers can proceed to develop reversible 4D printing of alloys. The challenges are low recovery strain, poor finishing, and poor mechanical properties. Although the development of the 4D printing of alloys may not move quickly in the near future, there is still a huge prospect for the 4D printing of alloys, which can be used in automation, electronic devices, biomedical devices, and even in daily applications.

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Compliance with ethics guidelines

Amelia Yilin Lee, Jia An, and Chee Kai Chua declare that they have no conflict of interest or financial conflicts to disclose.

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