1. Introduction

The general advantages of additive manufacturing (AM) have been extolled by numerous authors [1–4]. However, one area where the advantages are still being explored, and are not as widely recognised, is using AM to generate materials with site-specific properties (MSP). By changing the material properties with position one can produce a more efficient engineering structure than would be possible with homogenous properties alone. Alternatively, without the use of MSP, engineers may be left with a choice to either use an advanced, and likely expensive, material for whole AM components when only a small section actually requires these properties, or redesign a less efficient structure. Examples of where it is desirable, or even necessary, for material properties to change with location can be found in both advanced engineering components and more common objects. Properties are typically altered by changing the composition, phases or microstructure with location.

While using AM to generate MSP is a relatively new opportunity, MSP have been used in advanced engineering structures for a number of years. In fact, depending on how strictly one wishes to define the concept of MSP, their development can be traced back millennia. One early, but still widely practised, method of manufacturing MSP is carburising, whereby the diffusion of carbon atoms is used to alter the carbon content and hardness of metallic materials. Ancient Egyptian axes, dating back approximately three thousand years, were carburised to produce a more than six-fold increase in the hardness of the material surface in comparison to the centre [5]. Similar to a modern kitchen knife, the hard but brittle cutting tip would remain sharper for longer, while the tougher internal material prevented fracture of the tool. Of course, in the years intervening between the manufacture of the axes and kitchen knives, huge steps forward in terms of manufacturing and properties of MSP have been made.

Travelling back even further in time, and turning our attention to the natural world, we find that MSP are the norm, and have been so for millions of years. Evidence suggests that fish 96 million years ago had scales which varied gradually in hardness with distance from the scale surface. Under biting attack from a rival or predator, the hard outer coating helped prevent penetration of the scale, while the softer material beneath dissipated the energy [6]. Natural structures almost invariably contain smooth variations in material properties to make best use of the raw material available. It is the authors’ belief that this is where the future of using AM to generate MSP lies. Rather than discrete changes between material properties, by gradually changing material properties from location to location a number of benefits can be derived. To summarise:

- Improved bonding between dissimilar materials [7].
- Mechanical stress concentrations can be reduced, increasing component life [8–10].
- Reduction in thermal stress caused by different expansion coefficients [11,12].
- Removal of the distinct boundary in material properties can reduce the crack growth rate through different materials [13].

Such materials are commonly referred to as functionally graded. A metal-ceramic composite, developed in Japan in the 1980s, is considered a major step forward in the application of functionally, and compositionally, graded material [14]. A rocket casing material was required to withstand a maximum temperature of 2000 K and gradient of 1000 K over 10 mm, without developing high thermal stresses. It was only by...
gradual change of material properties could a suitable component be manufactured. In addition to aerospace, other potential applications of MSP are found in biomaterials, defence, energy conversion and many other fields [15, 16].

The gradient of the property change is of great importance in determining the overall behaviour of MSP. Possible gradients between distinct material properties/compositions are shown schematically in Fig. 1 and examples of each will be highlighted later. The most obvious transition between two compositions is the discrete version shown in Fig. 1a, comparable to a dissimilar metal weld. However, such a boundary is rarely achievable in practice, due to factors such as mixing of alloys in a melt pool, and may lead to undesirable effects; for example, DuPont reviews the issues associated with dissimilar ferrite to austenitic welds [17]. A gradual transition from one alloy, element or phase, to another shown in Fig. 1b is often favourable. The actual gradient following manufacture will be dependent on the thickness of deposited material layer, melt depth and the control with which the composition can be controlled. Alternatively, the material composition can switch between two or more different compositions at different locations as shown in Fig. 1c. On other occasions it may be desirable or even necessary to have more than two compositions (Fig. 1d). This could be utilised to exploit the different properties or avoid formation of unfavourable phases caused by the mixture of alloys B and C. Finally, with a great enough differential in melting temperatures, a metal matrix composite can be formed with a change in the density of insoluble powder particles in the matrix (Fig. 1e).

The advantages of MSP have led to them being regarded by some as the pinnacle of the modern material hierarchy [18]. Others have suggested that the current ‘holes’ in maps (stiffness/yield strength against density) of available materials may be filled by use of materials which combine two phases of differing properties. For example, Ashby [19] showed that in a sandwich panel, with a low density core and stiff outer sheets, can effectively fill requirements for high specific strength/stiffness materials. Similarly, lattice structures, where the absence of material could be considered the second phase, can provide relatively high mechanical properties for the low density region they occupy; one potential use is as the core of a sandwich panel. It should be noted that with such materials the geometric arrangement of the two phases is of critical importance in determining the overall material property [19, 20], and thus careful consideration must be given to both the tolerances in the design and accuracy of manufacture of such structures to ensure they meet the requirements.

In addition to the issue regarding tolerances alluded to above, there are a number of other challenges facing MSP before they can be widely adopted into industrial use, not least the higher costs associated with their manufacture, either by AM or other methods. This paper will highlight some these challenges and, where possible, potential routes to overcome them. First though, some of the recent progress in producing MSP by AM is summarised in order to provide context to the challenges that are faced by the technology.

2. Additive manufacturing of material with site-specific properties

While AM is the focus of the discussion presented here, it is important to realise that it is only a subset of possible methods for manufacturing MSP. The multitude of possible different manufacturing techniques are discussed elsewhere [5, 21, 22]. However, the very nature of AM, where material is added layer by layer, means that, in principle, any AM technique could be used to develop a graded structure with properties that vary with location. If all that is required to generate the desired site-specific properties is a change to the heat input strategy, then any AM technique may be as equally useful in their production. On the other hand, if compositional changes are required then some AM processes are inherently more favourable for MSP manufacture. Systems where the feedstock is locally introduced are more easily adaptable for the manufacture of MSP with varying composition, henceforth denoted MVC. For example, the multiple powder feeders arranged around the laser in the direct laser deposition (DLD) system allow a huge number of combinations of both composition and its gradient by dynamic control of the feedstock [23].

A variant of DLD, the laser engineered net shaping (LENS™) process, has been used in an attempt to vary the material composition in the ways illustrated schematically in Fig. 1a & b [24]. By attempting to generate a discrete boundary between two alloys (Fig. 1a), one potential issue with MSP has been highlighted. Despite a discrete change in powder feedstock, the transition between the two chemistries was blurred due to the re-melting of previous layers. Transport of material in the melt pool from the fraction of the re-melted layer into the newly deposited layer meant that it took three layers before the chemistry had completely changed. It is clear therefore that the chemistry of the feedstock does not necessarily correspond exactly to the final spatial distribution of chemistry within components. Thus, when designing components there must be a tolerance in the allowable chemical distribution.

Further considerations of the chemistry must be made if AM is used to generate alloys in-situ. Again the LENS™ process provides an example, this time consisting of two builds, one mixing powders of elemental titanium with niobium and another titanium with chromium [25]. The positive enthalpy of mixing of the Ti-10 at.%Nb solidified the solification and resulted in a poorly mixed, inhomogeneous alloy, whereas the negative enthalpy of mixing of the Ti-10 at.%Cr resulted in better mixing and faster solidification. Thus demonstrating another factor that must be accounted for when AM is applied to MVC.

The LENS™ process has also been used to exploit an often overlooked use of MVC [26]. By altering the flow rate from two powder hoppers during a build the composition was smoothly altered from pure titanium to titanium with 25 wt.% vanadium. What makes this work distinct from the other examples mentioned is that, rather than trying to use changes in material property to produce a more efficient engineering component, the intention was to gain understanding of the effect of alloying elements on phase transformations and microstructural evolution in α + β titanium alloys.

Unfortunately, not all compositions can be so easily transitioned between. Hofmann et al. [27] suggested that phase diagrams should be examined to find which phases are likely to appear at the interface between alloys. A multi-component phase diagram can give clues as to whether any unfavourable phases will be generated during manufacture. They showed that Ti-6Al-4V could be successfully transitioned to pure vanadium without the formation of brittle phases. In contrast, attempts to build components varying from titanium to Invar or stainless steel failed due to the material cracking during AM. Yet another factor to consider when designing MSP is exemplified.

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Fig. 1. Schematic diagram of potential material composition/property transitions. Redrawn from the examples provided by ref. [23].

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the material were determined by both hardness profiles and EBSD maps to have a distinct boundary. The fine grained material was reported to have a higher yield strength and Young’s modulus, and digital image correlation confirmed a non-uniform strain distribution when tensile testing this MSP [30]. This distribution of different microstructures could allow sections of components to be optimised for different conditions, for example creep or high strength. Alternatively, the thicker layers and greater beam speed associated with the higher laser power could be used to increase the material deposition rate to lower manufacturing costs while still achieving high strengths in certain regions with stricter requirements.

The possibility of generating a discrete boundary by altering the melt strategy is in contrast to the unintentional grading encountered when the feedstock was rapidly changed. The single alloy precludes material transport blurring the boundaries, and the heat affected zones are likely to be small. This suggests that tighter control of site-specific properties is achievable by variation of the melt strategy alone, but may not lead to as dramatic changes in the properties.

More success in near discrete changes to material composition have been achieved using ultrasonic AM (UAM) [31]. One example of UAM, where thin sheets are ultrasonically welded together, to generate MVC is that of iron-gallium wires being inserted into an aluminium matrix. No diffusion between the two materials could be identified in regions analysed by energy-dispersive X-ray spectroscopy, which, while not excluding the possibility of solid-state welding occurring at other locations, suggests that mechanical interlocking through friction was an important means of transferring load between the two materials. The increase in the elastic modulus of iron-gallium when magnetised allows the composite structure to have a tuneable stiffness, depending on the volume fraction and magnetic field. Materials with low thermal expansion, but lower density than Invar, have also been manufactured by UAM, this time by inserting shape memory alloys within an aluminium matrix. The smart structures illustrated in this paragraph show some novel applications for MVC.

Single composition structures can exhibit large changes in material property by altering the relative density or morphology of lattice structures [19,32]. Fig. 3 shows an example where, by altering the density, layers of differing stiffness and yield strengths were combined to generate a structure with properties that varied with site. The properties of each layer were similar to that of a homogeneous lattice of corresponding architecture and density, while the overall elastic modulus could be estimated by the rule of mixtures for the iso-stress condition [33].

Lattice MSP have already found an application as orthopaedic implants. It is notable that human bone is also a MSP, with a stiff outer region ($E \approx 20$ GPa) and spongy centre ($E \approx 0.5$ GPa) [34]. Stiff, single

**Fig. 2.** A hypothetical ternary phase diagram illustrating two available routes between compositions ((i) to (ii)). Redrawn from the example provided by ref. [23].

With intelligent design of the transition, one may be able to avoid these undesirable phases. Fig. 2 shows a schematic of multi-component phase diagram, with two desired compositions ((i) and (ii)). Clearly a direct interface (linear path) between the two would generate a brittle phase and a build failure or low quality component. However, by increasing the fraction of another constituent (Fig. 1d), which may not have the desired characteristics and make up only an inconsequential volume, the brittle phase can be avoided by following some arbitrary path [23].

This methodology was used to improve the quality of Ti-6Al-4V deposited on a stainless steel plate [28]. Without an interface layer, brittle intermetallics and residual stresses led to delamination and an unsuccessful build. Conversely, when a thin ($\approx 750$ μm) layer of NiCr was deposited between the two desired alloy systems, these issues were reduced and it was possible to successfully build the MVC.

By word of caution, it is worth noting that phase diagrams are based on the equilibrium phases encountered. During AM, where cooling rates can be very high, non-equilibrium phases may form which is not considered by such an approach. Further, the transport of material during remelting of layers may result in the actual path deviated from the intended one so care must be taken to ensure that the composition does not stray back into the region associated with brittle phases.

While powder bed systems are more difficult to dynamically control the chemistry during a build, they have been used to build MVC. The spreading of single composition layers limits the chemistry variation to the build direction. Further, standard commercial powder bed systems often contain a single powder hopper which makes changing the feedstock during a build a laborious task. However, selective laser melting (SLM) has been used to bond a zirconia thermal barrier coating to Waspalloy® [29], in a similar fashion to the schematic given in Fig. 1e. Unfortunately, the different material properties of the two components, combined with buoyancy and Marangoni effects in the melt pool, meant that while the deposited material was smoothly varied from 0% to 10% zirconia, the built samples contained regions of high and low volume fraction distinct from the intended gradient. In addition, it was necessary to alter the laser melt parameters during deposition to ensure satisfactory relative density.

Melt strategies can also be altered to change the material properties without changing the chemistry. SLM of a stainless steel alloy was conducted with two laser powers (1000 W and 400 W) but the energy density was kept uniform. It was found that the regions melted with the higher power exhibited both larger grains and stronger texture than those melted with the lower power. The two separate regions in

**Fig. 3.** Secondary electron SEM image of a graded lattice. Numbers 1–3 correspond to the smallest to the largest strut thickness. Reprinted from ref. [33].
property implants tend to shield bone from mechanical stress. Coupled with bones ability to react and reconfigure to the applied stress, this can lead to the bone weakening and the implant loosening and subsequently failing. AM lattice MSP could restore better function and aesthetics than currently possible by optimising properties for individual patients [34]. Fig. 4 shows an example of such a lattice, made with the powder bed electron beam melting (EBM) AM process. Despite the single alloy composition (Co-29Cr-6Mo) the mechanical properties are tailored to the site-specific demands by control of the lattice structure. This is a good example of AM being used to manufacture complex components that would be very difficult to produce by other methods and has been implemented into production. Since European certification was granted in 2007, thousands of AM MSP have been implanted in to patients [35].

3. Challenges to materials with site-specific properties

Apart from the orthopaedic implant just mentioned, MSP produced by AM has thus far been almost exclusively demonstration pieces, often used to highlight the potential benefits that may be possible in the future. Unlike MSP produced by conventional methods or even single alloy AM, there has been little uptake by industry. What follows are, in the authors’ opinion, the key challenges that must be overcome before this technology can be harnessed to derive the multitude of possible benefits. These challenges are interwoven and are unlikely to be solved individually: rather, a holistic approach is required, where the solution to one challenge informs the approach used to tackle another.

3.1. Defining the optimum material property distribution

When producing MSP by AM there is often a gradient between the properties rather than a discrete interface, the advantages of such an approach were highlighted in the introduction. However, typically the currently available studies do not give a reason for the choice of gradient they have used. Instead, it is simply decided almost arbitrarily with little consideration of the effects of a steeper or shallower gradient. Changing the gradient would influence both the manufacture and the properties of the material. This leads to perhaps the most pressing challenge; how to determine the optimal spatial distribution of material properties. While some regions may have required properties (thermal, mechanical, etc.) that are fixed and cannot be altered without compromising the part integrity, there are likely to be regions where there is a decision to be made regarding properties and thus manufacturing route. This decision will be complex and require knowledge of the material and manufacturing constraints, as well as the in service demands. For example, determining the arrangement of a high strength material with a separate thermal insulating phase will depend upon, among other factors, any transition phases, how quickly and controlled can the properties be varied, and the mechanical/thermal loading. Pure stress/thermal based modelling, assuming perfect bonding between the different sites, may suggest a discontinuous transition is favourable, however, material/manufacturing limitations could rule this out. A transition of properties between two sites is often required, which of course need not be a linear gradient between the two. The possible arrangement of the phases are almost limitless and design rules need to be established. Increased difficulty also arises when deciding overall component geometry due to variable material properties. For instance, the design of a load bearing beam is more straightforward when the material has uniform mechanical properties than when the properties can be varied between two extremes. If designing smart structures, such as the tuneable stiffness composite manufactured by UAM, then even further factors must be considered.

Of course, it is not necessary to only include a single transition. It has been demonstrated that DLD can be used to switch back and forth between two materials [36] (shown schematically in Fig. 1c). MSP on a small scale could also allow two phases of different properties to be combined to generate a composite with controllable properties. The continuously increasing computational power available to researchers allows an ever greater number of potential microstructures to be analysed. In one example, 7168 different arrangements of a hard and soft phase were analysed by the finite element method (FEM) [20], to examine how different microstructures (geometries and proportions of the different phases) influenced the overall stiffness, strength and toughness of the material. Some arrangements of the phases were more favourable than others, and these were used to construct tertiary diagrams allowing engineers to specify the required mix of properties and then read off the required arrangement of the phases. This is an exciting development in itself, and when combined with the benefits available by grading the properties on the larger macroscopic scale it becomes an even more appealing prospect.

3.2. Predicting the material properties of manufactured components

We have assumed above that the material properties are both known and can be controlled. However, when joining a high and low strength material it is not inevitable that the material strength will vary linearly between the two values. The changing material properties brought about by changes to the microstructure must be measured and quantified. Of course, it is not possible to measure the property at all locations between the two sites, and neither would such an approach be useful to model the response of the structure. Instead, idealisations of property variation based on measured values must be used. When concerned with fracture mechanics, engineers often use the exponential law idealisation, whereas when conducting stress analysis the power

Fig. 4. A Co-29Cr-6Mo alloy femoral knee implant fabricated by EBM. Reprinted from ref. [35].

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law is more commonly applied [18]. Another possible route is through the use of material elements or ‘maxels’, which would allow an engineering design to be built up from small finite blocks, each with the potential to have different properties. These need not be each defined manually, rather a smooth function could be defined and discretised into separate values automatically, similar to how a smoothly varying geometry is discretised into layers during standard AM. Assuming that the material contains no weak interface, such an arrangement of elements could then be analysed using FEM. Of course, any additional phases generated by the interface between different sites must be identified as they could result in a step change in properties. Predictions based on individual phase properties may be inadequate if there is any weak bonding between phases.

### 3.3. Material selection

Even when the exact properties required at each location are defined, the material used to achieve this must be chosen. If the objective is to alter the properties through the melt strategy alone, then an alloy must be chosen to make this possible, plus strategies developed to get the required properties. While this is no small task, if multiple compositions are to be used the situation becomes even more complex. All neighbouring compositions must be compatible, and not lead to undesirable phases/properties at the transition. If, for example, brittle phases or thermal or mechanical, such as macrosegregation of solutes during solidification, and technical, like poor process control. In-situ monitoring of the phases and chemistry during the build may provide a solution, or at least more information about the effect. If a feedback loop were to be implemented, it may even allow correction of composition issues during manufacture. Of course, some methods, such as using a single alloy and varying the properties through heat input strategy alone [30] or UAM, where little material transport has been reported [31], are less susceptible to these issues.

### 3.4. Understanding differences

Many of the studies of MVC produced by AM have found that the distribution of chemical components, and thus material properties, of the manufactured parts deviates somewhat from the intended. Clearly the reasons for this must be identified and could include the physical, such as macrosegregation of solutes during solidification, and technical, like poor process control. In-situ monitoring of the phases and chemistry during the build may provide a solution, or at least more information about the effect. If a feedback loop were to be implemented, it may even allow correction of composition issues during manufacture. Of course, some methods, such as using a single alloy and varying the properties through heat input strategy alone [30] or UAM, where little material transport has been reported [31], are less susceptible to these issues.

### 3.5. Defining tolerances

Following from above, it seems probable that, at least in the short term, the material properties of MSP/MVC will be less predictable than engineering alloys of uniform composition. Property tolerances may have to be redefined that include not only the overall variation in components, but also local variation. In addition to ensuring the correct properties at specific locations, there may be requirements arising from the transition from one property to another, for example to avoid any sharp changes in properties. If the control of the material property with site is insufficient to hit these targets, then MSP may not be appropriate. On the other hand, if poor control means the tolerances must be set high, then some of the benefits of MSP will be reduced and may lead to a situation where a theoretical analysis suggests benefits, but once tolerances are accounted for they are removed. The importance of manufacturing being considered during design is thus highlighted.

### 3.6. Software limitations

Currently most computer aided design (CAD) software defines components in terms of their geometry alone. The most common type of AM CAD file, STL’s, only defines the surfaces of a model with no information regarding material. This is unsurprising given the relative scarcity with which MSP are encountered in engineering components. Before MSP can be properly adopted into engineers’ toolboxes CAD programs and files must be updated to allow material properties to be defined in a continuous or non-discrete manner. If CAD models were defined in terms of the maxels mentioned earlier, on transfer to the AM equipment this could result in changes to the melt strategy, composition, etc. during the build. Such a material based model should also help with modelling the manufactured component. Similar to CAD packages, commercial FEM software typically defines materials discretely. Allowing maxels to be transferred from a CAD package to an FEM package could aid the development of useful models of MSP. Of course, such models rely on the properties being predictable, mentioned earlier.

### 3.7. Expanding the capability of lattices

It is possible to generate lattice structures and then fill the surrounding with a different material. Such composites may be able to exploit the advantages of both phases/microstructures. One such example is the use of steel lattice structures to slow the velocity of projectiles. Ceramic inserts, which fragmented but were contained by the lattice upon impact, were able to completely arrest a high speed projectile [37]. In this case the ceramic was inserted into the lattice following manufacture, but AM may allow MSP with such a contrast in phase properties to be built in a single step. Alternatively, different manufacturing techniques could be combined to generate a composite of different phases/microstructures. For example, EBM lattices were filled with powder and subjected to spark plasma sintering to generate a titanium component with different microstructures but excellent bonding between [38].

### 4. Summary

MSP hold great promise to allow more efficient engineering structures, with applications in a whole host of engineering disciplines. Components with site-specific properties allows different regions to be optimised for the dissimilar conditions they experience, and prevents having to build an entire part from a prohibitively expensive material just to satisfy the conditions at one location. The transition from one set of material properties to another is of crucial importance in determining not only the manufacturability of the component, but also the overall response of the component to loading. Having a smooth transition from one set of properties to another can avoid the problems associated with a discrete interface. In addition to the direct exploitation of the tailored material properties, for mechanical benefits or thermal or corrosion protection, MVC by AM can be used to quickly explore phase diagrams by manufacturing material with numerous, spatially varied, compositions. Other methods are available to manufacture MSP, but AM offers potential new routes and may allow greater control than previously possible. Before any advantages can be realised however, there are issues that must be addressed. These include material, structural and software engineering, for example determining the ideal property distribution, predicting the material response and updating CAD software to allow non-discrete material definitions. Some engineering judgement may be required when determining the tolerances as to the material property variation with position, which in the studies published to date has often shown some variation from the intended. In time, and with better understanding of the manufacturing processes, the aim should be to minimise these variations.
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