

## REVIEW ARTICLE

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# Corrosion of metallic materials fabricated by selective laser melting

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Additive manufacturing is an emerging technology that challenges traditional manufacturing methods. However, the corrosion behaviour of additively manufactured parts must be considered if additive techniques are to find widespread application. In this paper, we review relationships between the unique microstructures and the corresponding corrosion behaviour of several metallic alloys fabricated by selective laser melting, one of the most popular powder-bed additive technologies for metals and alloys. Common issues related to corrosion in selective laser melted parts, such as pores, molten pool boundaries, surface roughness and anisotropy, are discussed. Widely printed alloys, including Ti-based, Al-based and Fe-based alloys, are selected to illustrate these relationships, and the corrosion properties of alloys produced by selective laser melting are summarised and compared to their conventionally processed counterparts.

*npj Materials Degradation* (2019)3:24; <https://doi.org/10.1038/s41529-019-0086-1>

## INTRODUCTION

Additive manufacturing (AM) is a key emerging technology that is challenging multiple manufacturing methods, and the principle of AM is the layer-by-layer addition of powders or liquids to fabricate an object.<sup>1,2</sup> To date, there are many metallic materials that can be printed effectively, and the existing AM technologies are divided into two main categories: powder-fed and powder-bed systems. The powder-fed category is further classified for direct laser deposition (DLD), laser engineered net shaping methods and so on,<sup>3–8</sup> while the powder-bed category involves selective laser melting (SLM), selective laser sintering and electron beam melting technologies.<sup>9–14</sup> In general, the cooling rate for SLM is usually  $>10^5$  K/s, which is higher than that of DLD (ranging from  $10^3$  to  $10^5$  K/s) and much higher than that for traditional casting methods that have an approximate solidification rate of 273–373 K/s.<sup>15–18</sup>

Huge effects have been paid over the past decades in the optimisation of printing devices, including highly reliable laser, inexpensive high-performance computing hardware and software. Currently, SLM has been highlighted for its unique advantages in producing metallic materials in comparison with other fabrication techniques.<sup>19–22</sup> SLM was developed in 2002<sup>23</sup> and this laser melting technique was originally used as a surface technology to enhance the mechanical properties and corrosion resistance of components.<sup>24–28</sup> The powder-bed technique has shown the admirable capacity to produce components with high accuracy, required material selection and excellent mechanical properties.<sup>29–31</sup> The SLM system utilises a focused laser beam, usually a Yb: YAG fibre laser, to melt the powder bed, and the powder is fed from a supply container as displayed in Fig. 1a.<sup>32–34</sup> The laser scan way is designed according to a computer-generated path and the printing process is repeated layer-by-layer by lowering the platform until the whole objects are totally fabricated and then the excessive powder is collected for recycling. There are many

factors that will affect the quality of the SLMed parts, including the laser power, scanning speed, powder size, powder type (argon- or nitrogen-atomised), powder layer thickness, scanning path, hatch space, etc., as shown in Fig. 1b. During the SLM process, the local rapid heating and fast cooling rates coupled with thermal cycling induce the formation of unique microstructures with refined grain structures, dislocation cells and internal residual stresses.<sup>35</sup> These conditions also cause the formation of metallurgical defects, including un-melted powders, micro-cracks, entrapped gas pores, balling, and the rough surfaces, as displayed in Fig. 1c.<sup>36–41</sup>

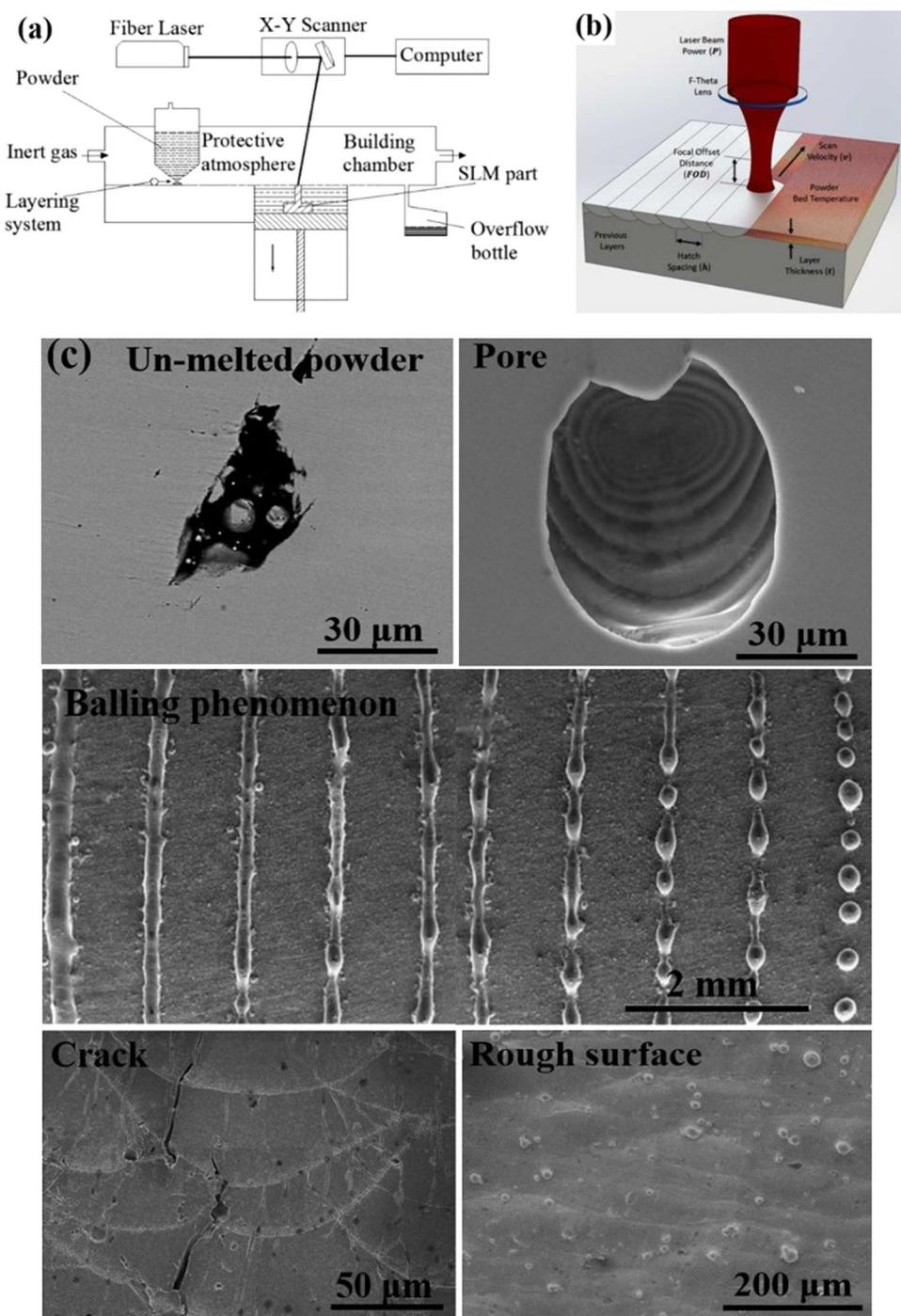
At present, only AlSi10Mg, TiAl6V4 and CoCr alloys, can be reliably printed,<sup>42–44</sup> whereas Fe-based and Ni-based alloys have been fabricated by SLM recently.<sup>45–49</sup> The quality of the printed parts from the SLM process is the most challenging issue to be resolved, and there may be multiple factors for this: (1) the rapid cooling rate during solidification results in the formation of non-equilibrium phases with a large range of compositions<sup>50–52</sup>; (2) the molten pool boundary inside the parts, as well as the pores, cracks and rough surfaces, can lead to a severe drop in plasticity. These sites could also be preferential areas for corrosion.<sup>53,54</sup> Therefore, researchers are acquiring comprehensive data regarding processing parameters and the corresponding printed materials. The effects of the printing parameters on the microstructure and defect evolution during rapid solidification are widely reported, and the optimised printing parameters can usually lead to better mechanical properties.<sup>55–57</sup> However, the corrosion behaviour and durability of the selective laser melted (SLMed) parts have not drawn considerable attention to date yet<sup>58–62</sup> and the understanding of the underlying corrosion mechanisms of the SLMed metals and alloys still remains in its infancy. It is well acknowledged that corrosion leads to an annual financial loss of US\$4 trillion globally due to corrosion damage and corrosion protection

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Received: 21 November 2018 Accepted: 15 May 2019

Published online: 11 June 2019



**Fig. 1** **a** Schematic diagram of the SLM system, **b** scanning strategy of a powder bed under laser irradiation,<sup>32–34</sup> and **c** metallurgical defects in the SLMed parts, including un-melted powder,<sup>36</sup> entrapped gas pore,<sup>37</sup> balling phenomenon,<sup>38</sup> micro-cracks<sup>39</sup> and rough surfaces.<sup>40</sup> (**a** adapted with permission from ref. <sup>32</sup>, copyright Elsevier 2006) (**b** adapted with permission from ref. <sup>34</sup>, copyright Elsevier 2018) (**c** adapted with permission from refs. <sup>36,37,40</sup>, copyright Elsevier 2018; <sup>38</sup> copyright Springer 2011; <sup>39</sup> copyright Springer 2017)

investment.<sup>63,64</sup> Thus, corrosion must be considered with regard to the service life of additive manufactured parts for the widespread application of this technology.

In this paper, we present a brief review of the published literature regarding a number of metallic alloys fabricated via SLM technology, combined with our recent work, to clarify the difference in corrosion behaviour between traditional manufacturing and the novel AM technique.

## COMMON CORROSION ISSUES FOR THREE-DIMENSIONAL (3D) PRINTED MATERIALS

### Pores

Pores first appear in powder metallurgy processes and also occur in the SLMed parts, which can affect the corrosion behaviour of the components.<sup>65</sup> Pores in stainless steels manufactured by powder metallurgy have been confirmed to reduce the passive property in the presence of sulphuric and phosphoric acid

solutions<sup>66</sup> and this may also be the case for the SLMed stainless steels. Typically, the pores in the SLMed parts are divided into two types: one type exists around the un-melted powders, and another is caused by the trapped gas inside the powders during gas atomisation.<sup>67,68</sup> The porosity can be reduced to a certain extent by optimising the printing conditions, including the laser energy, scanning rate and scanning direction. Sander et al.<sup>69</sup> found that increasing the laser power or decreasing the scanning rate properly can reduce the porosity of the SLMed 316L stainless steel. A similar tendency was also obtained for the other metals, such as nickel-based and aluminium-based alloys.<sup>70,71</sup> A more quantitative way to assess the effect of printing parameters on porosity within components is using the volumetric energy density ( $E_v$ ) calculated via Eq. (1), which describes the average energy per volume of powders<sup>72,73</sup>:

$$E_v = \frac{e}{rdt} \quad (1)$$

where  $e$  is the value of laser energy,  $r$  is the scanning rate,  $d$  is the hatch distance and  $t$  is the thickness of the powder layer. Han et al.<sup>74</sup> defined the process windows of 120 to 202 J/mm<sup>3</sup> to build Ti6Al4V parts with a porosity <0.1%. The laser energy density for the lowest porosity (~0.3%) of the SLMed 316L stainless steel was around 105 J/mm<sup>3</sup> in Fig. 2a<sup>75</sup>, for the SLMed AZ91D magnesium alloy, the process window for the highest relative density was in the range from 83 to 167 J/mm<sup>3</sup>,<sup>76</sup> the laser energy density for the lowest porosity (around 0.8%) of the SLMed CoCrFeNiMn high-entropy alloy was ~60 J/mm<sup>3</sup> in Fig. 2b<sup>77</sup>; while the laser energy density for the lowest porosity (around 3.0%) of the SLMed Al-12Si alloy was around 30 J/mm.<sup>3,78</sup> However, several authors doubted the availability of the energy density as an assessment criteria of the porosity, and they pointed out that some other printing parameters, such as hatch style and laser diameter, were disregarded, which can also affect the porosity.<sup>79</sup> Further investigations should be conducted systematically to clarify the relationship between the porosity and processing parameters.

Pores can somewhat compromise the pitting corrosion resistance of the matrix, and an immersion test for the SLMed 304L and 316L stainless steels in ferric chloride solutions showed that the main corrosion attack occurred within the pores.<sup>65</sup> The authors ascribed this preferential corrosion to local acidification inside the pores, leading to de-passivation of the stainless steel substrate and this process was accelerated by the cathodic activity outside the pores.<sup>80</sup> Moreover, Schaller et al.<sup>81</sup> used a micro-electrochemical test and noted that a reduced pitting corrosion resistance of the SLMed 17-4 PH stainless steel occurred at pores with diameters that were larger than 50 µm, whereas a passive condition still occurred when the pore size was smaller than 10 µm.

Pores with diameters below 10 µm in the SLMed 316L stainless steel were still corroded in more aggressive environments, such as high-temperature sulphuric acid.<sup>82</sup> Pore geometry also had a substantial effect on the pitting corrosion behaviours and irregularly shaped pores were deemed to corrode easily due to the enrichment of aggressive ions at the corners. However, the size distribution of the pores in the SLMed parts has not been evaluated systematically in the existing literature and further understanding of the effect of porosity, such as pore size and aspect ratio, on the degradation behaviours of the SLMed parts needs to be clarified. Moreover, the post heat isostatic pressing for the SLMed parts can usually remove pores, and the related effects on corrosion properties are complex and were not discussed in this study. Adding some minor alloying elements to enhance the interfacial bonding force is another method to reduce the porosity in the SLMed parts, such as secondary particulates to produce crack-free high-strength aluminium alloys.<sup>39</sup> Yusuf et al.<sup>83</sup> also adopted high-pressure torsion plastic deformation to reduce the

porosity, and continued efforts in this regard are needed in the future.

#### Molten pool boundaries (MPBs)

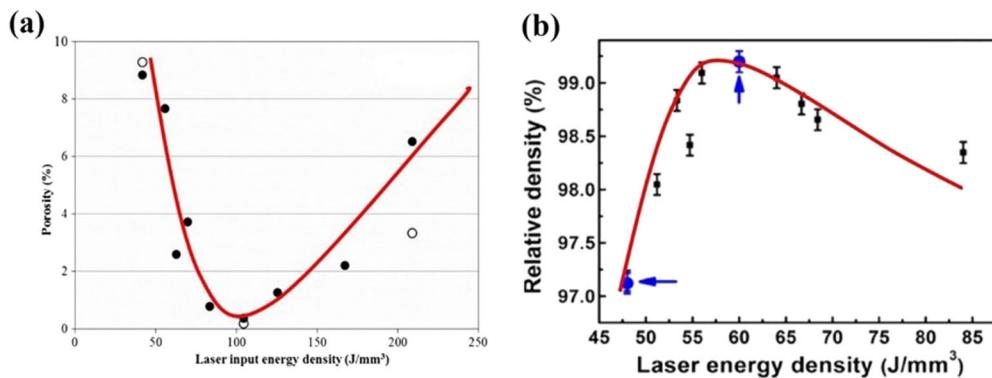
MPBs are widely present in the SLMed alloys and several authors<sup>84,85</sup> have noted that elemental segregation, thermal stress and non-equilibrium phases can exist at the MPBs. Actually, the MPBs can be divided into two categories: layer–layer MPB and track–track MPB, as displayed in Fig. 3a.<sup>53</sup> Two ends of the track–track MPBs connect with layer–layer MPBs, resulting in sharp angles between the two types of MPBs, and these sharp angles would greatly affect the mechanical properties, especially the plasticity.<sup>53,54</sup>

As a non-equilibrium region, selective penetrating attack might occur at the MPB sites preferentially. For the SLMed AlSi10Mg alloy, isolated silicon particles can gather inside the melt pool borders.<sup>86–88</sup> It is well-recognised that silicon is cathodic with respect to the aluminium matrix, which may lead to the formation of micro-galvanic couples, resulting in localised corrosion phenomena.<sup>89,90</sup> Meanwhile, the corrosion rate of Al–Si alloys was verified to increase with increasing silicon content in a 0.5 M NaCl solution at 25 °C.<sup>91</sup> Thus, this unique microstructure caused a selective attack to occur along a preferential path at the MPBs for the SLMed AlSi10Mg alloy as displayed in Fig. 3c. However, this composition segregation phenomenon at the MPBs was not obvious for Fe-based alloys, such as 316L stainless steel, but those sites were still preferentially corroded compared with the wrought counterpart as shown in Fig. 3d, e, which should be attributed to the large interfacial stress and micro-voids at the MPBs.<sup>92,93</sup>

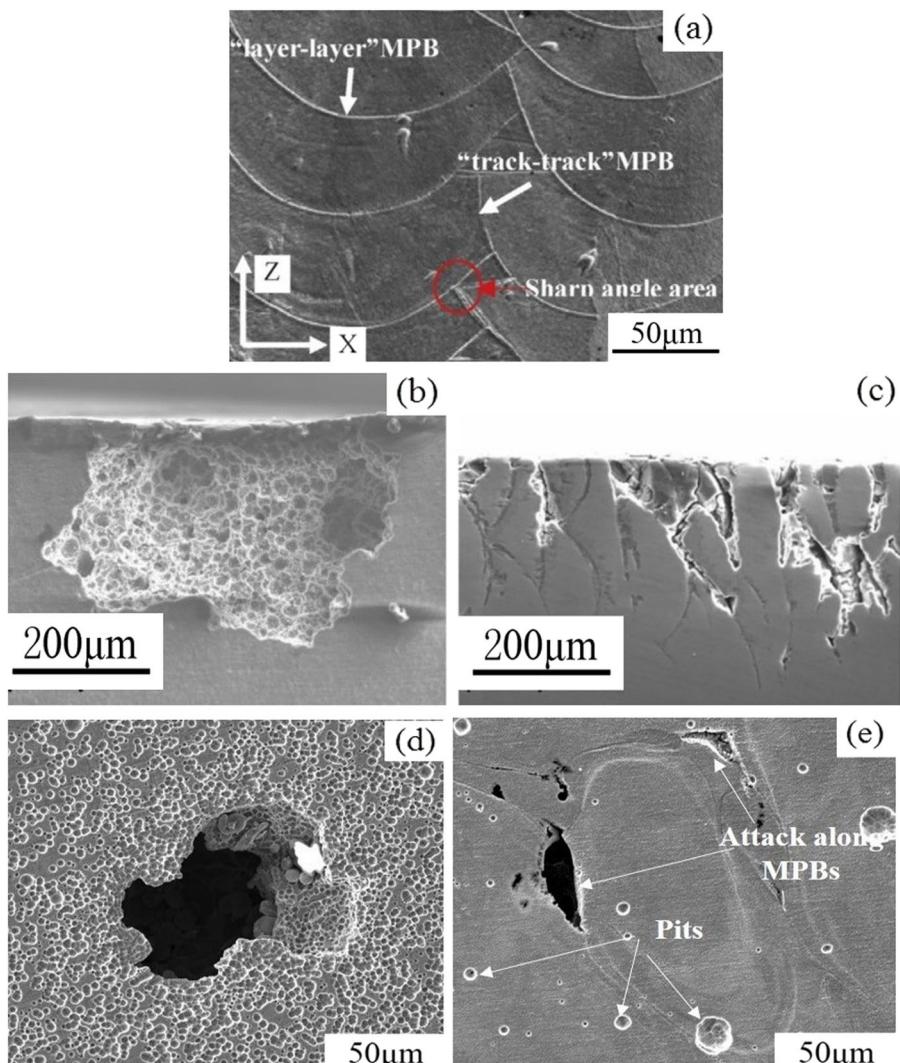
#### Surface roughness

The surface roughness of the parts fabricated by SLM is usually higher (range from 10 µm to 30 µm) than that in parts manufactured by other methods, such as milling (~1 µm).<sup>94</sup> There are two main reasons for the rough surface in the SLM process, one is caused by evaporation and the Marangoni force existed during the powder melting. The gas expansion destabilises the melt flow, and a highly irregular and unstable melt pool increases the surface roughness and porosity.<sup>95–99</sup> With thick powder layers, more powder materials are melted by the laser beam and more gas expansion occurs.<sup>96,100–102</sup> Thus, the surface roughness could be decreased to some extent with a small layer thickness, as displayed in Fig. 4a. However, it is time-consuming to finish a component comprising thin layers. A second reason for the rough surface is improper powder melting and the balling phenomenon (the formation of metallic droplets in opposition to a desired uniform spread of liquid metal on the molten surface during laser melting).<sup>103,104</sup> When a low laser power is setup, the delivered energy is insufficient to melt the powder particles completely and the solid powder particles adhere to the surface of the component. Therefore, it is expected that surface roughness can be minimised with an increase in the heat input, because a higher heat input value can flatten the melt pool, improving the interlayer connection due to the keyhole effect and increasing the wettability of the melt, as displayed in Fig. 4b.<sup>105</sup> Improved wettability can reduce the melt pool tendency to undergo balling by relieving surface tension variations, thus reducing the roughness.<sup>106</sup> However, a very high heat input can be detrimental to the surface finish due to the increasing recoil pressure that disrupts the molten pool surface.<sup>107</sup> Finally, large powders (larger than 100 µm) are difficult to melt due to the relatively small laser spot diameter (usually range from 50 to 100 µm<sup>108,109</sup>), which might lead to poor surface finish, as shown in Fig. 4c.<sup>35</sup>

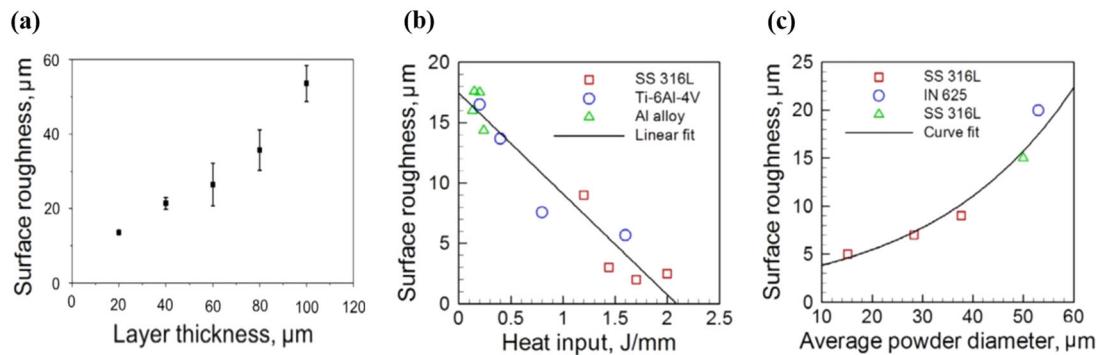
Generally, surface conditions play an important role on the corrosion properties of materials involving interfacial reactions with the environment. Pitting susceptibility<sup>110</sup> and general corrosion rate<sup>111</sup> all increased with the increase in the surface



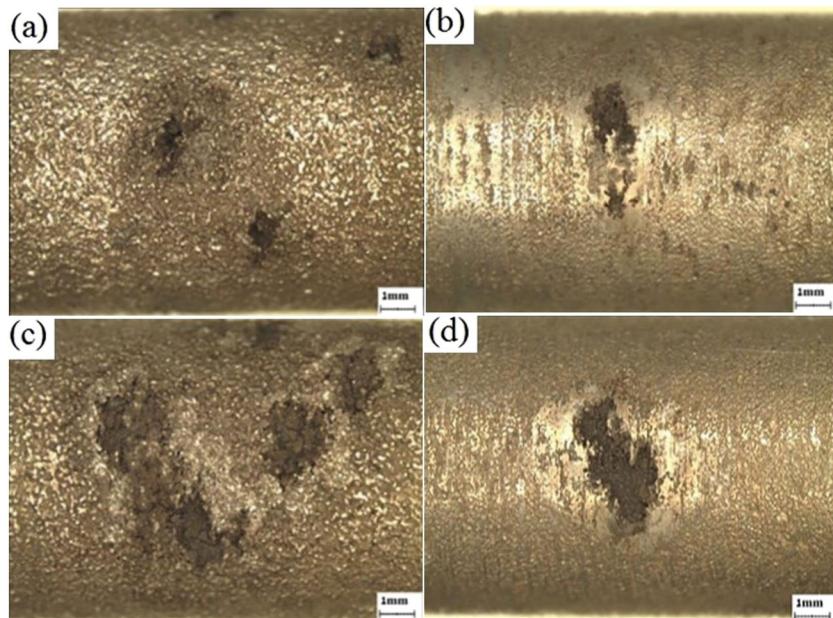
**Fig. 2** **a** porosity of the SLMed 316L stainless steel at various energy densities<sup>75</sup> and **b** relative densities of the SLMed CoCrFeNiMn high-entropy alloy at various energy densities.<sup>77</sup> (**a** adapted with permission from ref. <sup>75</sup>, copyright Springer 2017) (**b** adapted with permission from ref. <sup>77</sup>, copyright Elsevier 2018)



**Fig. 3** **a** Scanning electron morphology of the MPBs in a SLMed sample,<sup>53</sup> cross-sectional corroded morphologies of **b** wrought and **c** SLMed AlSi10Mg alloy in NaCl solution,<sup>206</sup> surface corroded morphologies of **d** wrought and **e** SLMed 316L stainless steel in ferric chloride solution.<sup>92</sup> (**a** adapted with permission from ref. <sup>53</sup>, copyright Elsevier 2014) (**b** and **c** adapted with permission from ref. <sup>206</sup>, copyright Elsevier 2016) (**d** and **e** adapted with permission from ref. <sup>92</sup>, copyright Springer 2019)



**Fig. 4** Relationship between surface roughness and **a** layer thickness,<sup>100</sup> **b** heat input<sup>105</sup> and **c** powder diameter.<sup>35</sup> (a adapted with permission from ref. <sup>100</sup>, <https://doi.org/10.1016/j.actamat.2015.06.004>, Creative Commons Attribution License) (b adapted with permission from ref. <sup>105</sup>, copyright Springer 2012) (c adapted with permission from ref. <sup>35</sup>, copyright Elsevier 2017)



**Fig. 5** Surface morphologies of the SLMed AlSi10Mg alloy after immersion in 3.5 wt.% NaCl solution: **a** as-received for 15 days; **b** polished for 15 days; **c** as-received for 30 days; and **d** polished for 30 days. (a-d) adapted with permission from ref. <sup>115</sup>, copyright Elsevier 2017)

roughness of stainless steels. A similar trend has also been reported for other metals, such as copper<sup>111–113</sup> and magnesium alloys.<sup>114</sup> The obtained results on the SLMed AlSi10Mg alloy in Fig. 5 indicated that the corrosion resistance of the polished SLMed parts was significantly improved compared to the as-received SLMed AlSi10Mg alloy. Localised corrosion attacks, such as pitting and cracking initiation, would preferentially occur at the irregular and roughness sites on the SLMed AlSi10Mg alloy caused by large amounts of cavities and other surface defects.<sup>95,115,116</sup> Meanwhile, the surface roughness could also be substantially affected the oxidation kinetics of the SLMed alloys, especially for the case of a sintered powder.<sup>117,118</sup> The parabolic constants of the oxidation kinetics at the initial stage for the SLMed Inconel 718 alloy under 850 °C were two times higher than those of ground samples due to the rough surface.<sup>40</sup>

Optimising the surface finish has been a tough challenge for 3D printing processes, such as for complex structural parts, where the powder is trapped within the mesh structure during the fabrication process and difficult to remove due to blind spots.<sup>119,120</sup> Thus, systemic work related to surface post-processing of AM-produced materials should be carried out because there are still a numerous knowledge gaps in this aspect.

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#### Anisotropy

The anisotropy in the SLMed parts is usually caused by the different solidification rates in different directions, and heat conductivity in the building direction (z-axis) is typically faster than that in the other two spatial directions (x- and y- axes) due to the high-heat transfer efficiency of the pre-deposited metals.<sup>121–123</sup> The micro-structural anisotropy in the SLMed parts usually leads to anisotropic mechanical properties<sup>124–126</sup> and corrosion behaviours.<sup>127,128</sup> For the mechanical properties, there was a larger elongation along the building direction than in the other two spatial directions due to the grain growth mainly occurring along the building direction, such as for stainless steels and CoCrW alloys.<sup>129–131</sup> Regarding the anisotropic corrosion behaviours in a Ti6Al4V alloy, the corrosion rates of the SLMed parts were relatively small and changed little with different research planes in chloride solution. However, in an aggressive solution, such as 1 M HCl, the XY-plane of the SLMed Ti6Al4V alloy showed a lower passive current density (approximately by half) than the XZ-plane in Fig. 6b,<sup>58</sup> which was attributed to the decreased amount of  $\alpha'$ -martensitic and the increased amount of  $\beta$ -phase on the XY-plane, as displayed in Fig. 6c, d. The metastable  $\alpha'$ -martensitic phase was formed under high-thermal gradients during the SLM

process and the acicular  $\alpha'$ -martensitic phase is in a high-energy state with regard to corrosion, which led to a decreased uniform corrosion resistance for the XZ-plane in an acidic environment.<sup>132</sup>

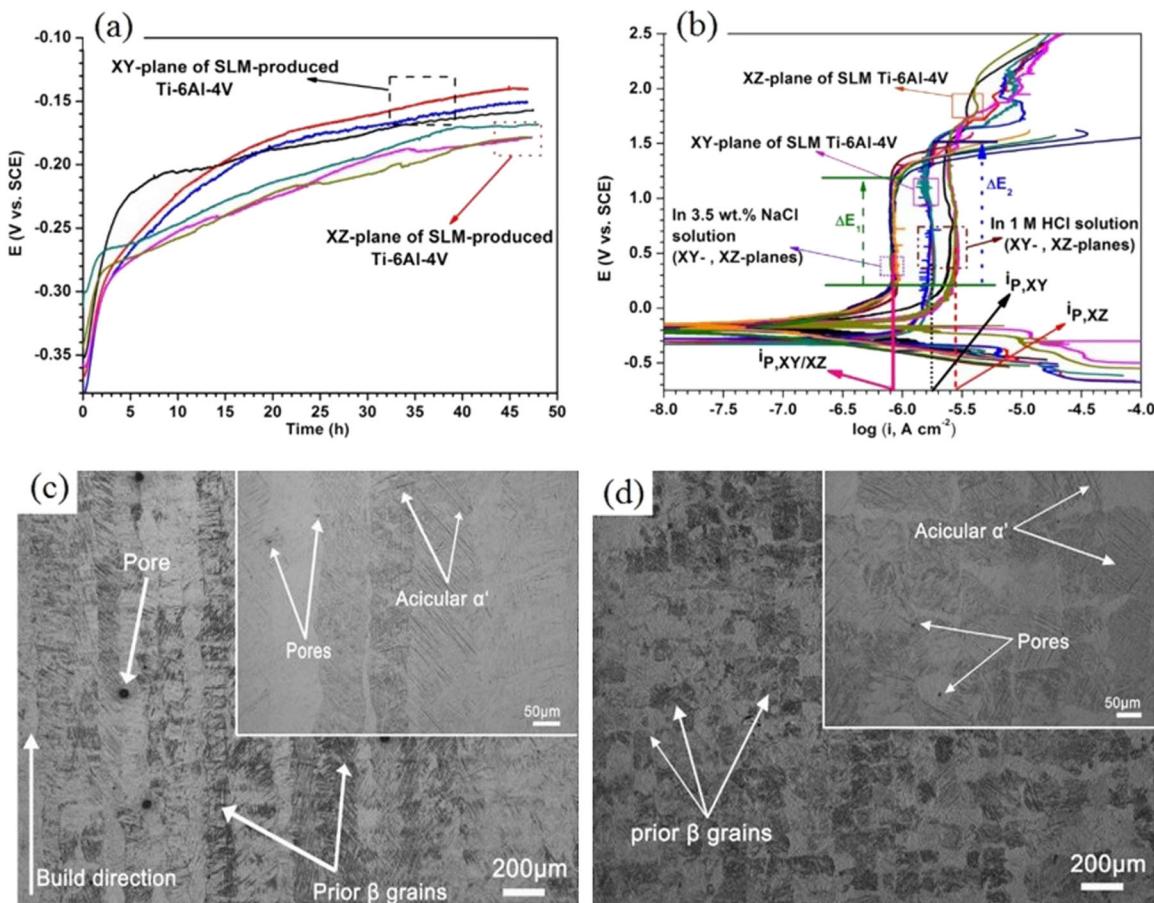
The distinction in the corrosion behaviour can also be attributed to the physical structures in the different planes, such as for Al-Si alloys<sup>127</sup> and nickel-based alloys.<sup>133</sup> The XZ-plane of the SLMed Al12Si alloy exhibited better pitting corrosion resistance compared with the XY-plane in chloride solution as displayed in Fig. 7a, b. The corrosion products on the XY-plane extruded the small-bore and deep Si shells on the substrate and the chloride ions continuously penetrated the aluminium substrate with the cracking of the Si shells, therefore, severe pitting corrosion was ultimately induced as displayed in Fig. 7c. However, the corrosion products deposited in the shallow and large-bore Si shells for the XZ-plane on the SLMed Al12Si alloy, and the undamaged Si shells and formed oxide film constituted a protective layer to protect the aluminium substrate from the further attack of chloride ions, thereby displaying excellent pitting corrosion resistance for the XZ-plane, as shown in Fig. 7d.

### SPECIAL CORROSION ISSUES OF SEVERAL 3D PRINTED MATERIALS

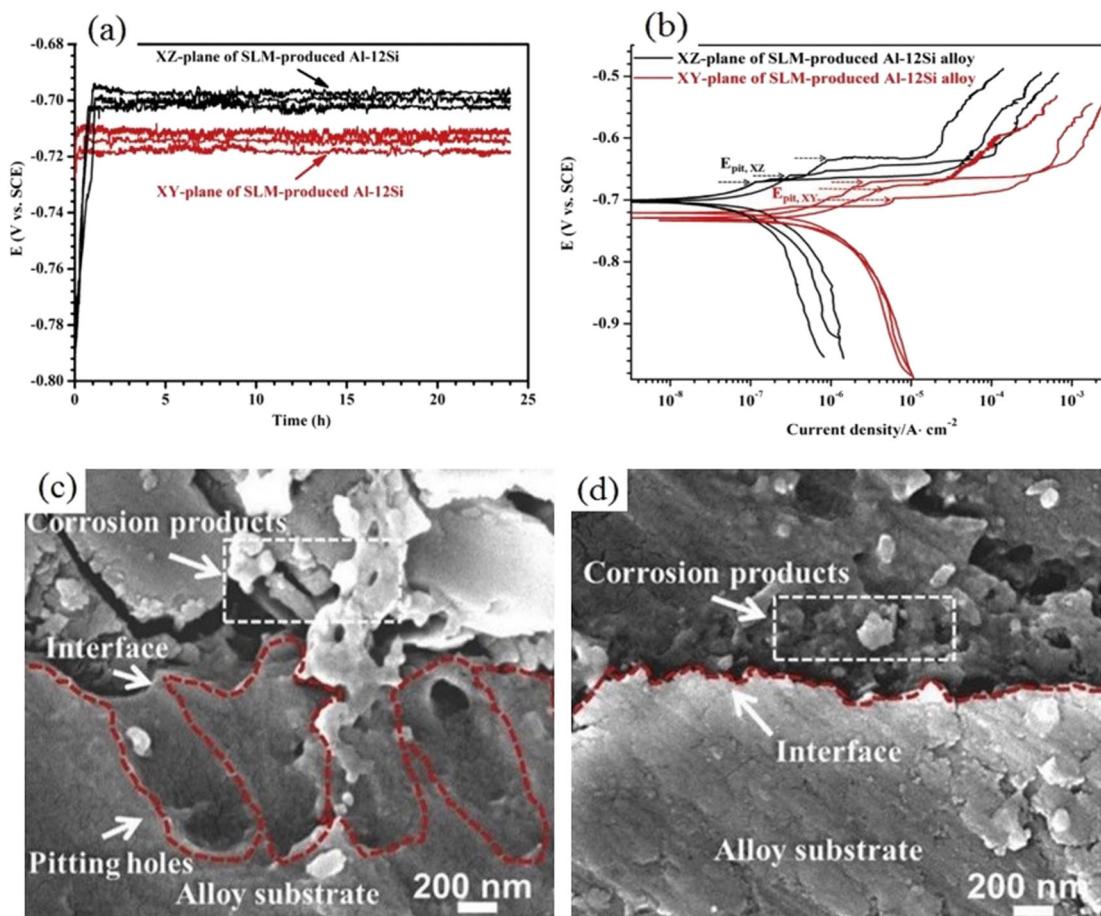
#### Ti-based alloys

As titanium combines broad industrial application in high-performance parts with high machining costs, hard moulding and a long lead time in conventional processing, titanium and titanium alloys are of utmost interest with regard to AM

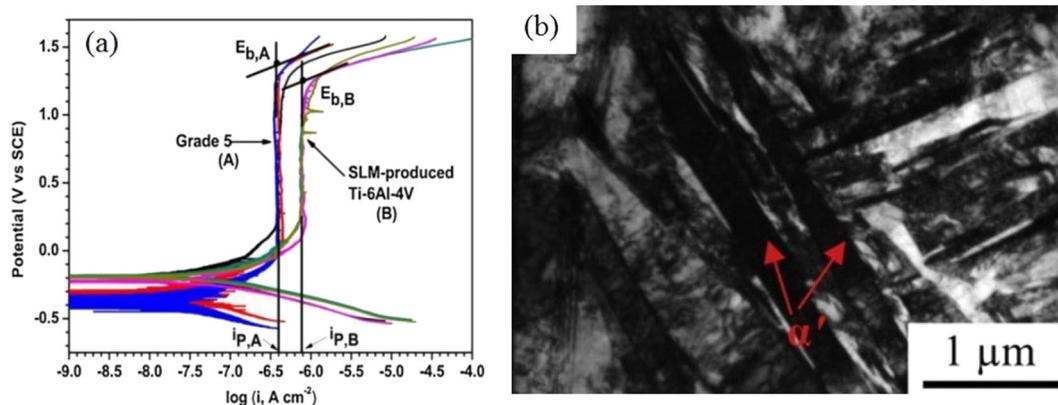
techniques.<sup>134–141</sup> By one calculation, a 50% reduction of production costs was reported for a wrought titanium alloy engine bracket using the AM method.<sup>142</sup> Among titanium alloys, Ti6Al4V is the most widely used material for many engineering parts and biomedical implants. A study conducted by Dai et al.<sup>132</sup> showed that the SLMed Ti6Al4V exhibited a higher passive current density and a lower pitting potential ( $\sim 150$  mV lower) in chloride solution compared to the wrought counterparts due to the existence of metastable  $\alpha'$ -martensite as displayed in Fig. 8a. The martensitic transformation occurred due to the very high cooling rate and the acicular  $\alpha'$ -martensite was well distributed throughout the microstructure, accompanied by some typical long and columnar prior  $\beta$ -grains, as shown in Fig. 8b.<sup>119,143</sup> Additionally, the volume fractions of the  $\beta$ -phase for the commercial and the SLMed Ti6Al4V alloy were about 13.3% and 5.0%, respectively.<sup>132</sup> It is known that the  $\beta$ -phase contains more V content and that the oxide film formed on the  $\beta$ -phase is more stable than that on the  $\alpha$ -phase, which plays an important role in improving its corrosion resistance.<sup>144</sup> Therefore, it is reasonable to conclude that the SLMed Ti6Al4V alloy exhibit poorer corrosion resistance compared to the commercial alloy.<sup>145</sup> The acicular  $\alpha'$ -martensite can vanish gradually and transform into  $\alpha$ -martensite with increasing heat-treatment temperature, therefore, a plate-shaped  $\alpha$ -phase and a lamellar  $\alpha + \beta$  mixture form continuously.<sup>146–149</sup> However, the grain size also increased after the heat treatment and weakened its passivation property, which overwhelmed the decreasing amount of the  $\alpha'$ -phase on corrosion resistance,<sup>150</sup> so the heat



**Fig. 6** **a** Corrosion potentials and **b** potentiodynamic polarisation curves for the XY- and XZ-planes of the SLMed Ti6Al4V alloy, microstructures of the **c** XZ-plane and **d** XY-plane of the SLMed Ti6Al4V sample.<sup>58</sup> **(a-d)** adapted with permission from ref.<sup>58</sup>, copyright Elsevier 2016



**Fig. 7** **a** Corrosion potentials and **b** potentiodynamic polarisation curves of the XY- and XZ-planes for the SLMed Al12Si alloy in the aerated 3.5 wt.% NaCl and SEM images of corrosion morphologies on **c** the XY- and **d** XZ-planes.<sup>127</sup> (**a–d** adapted with permission from ref. <sup>127</sup>, copyright Elsevier 2018)



**Fig. 8** **a** Potentiodynamic polarisation curves for the SLMed Ti6Al4V alloy and commercial Grade 5 alloy in 3.5 wt.% NaCl solution<sup>132</sup> and **b** bright-field TEM image of the as-received SLMed Ti6Al4V alloy.<sup>119</sup> (**a** adapted with permission from ref. <sup>132</sup>, copyright Elsevier 2015) (**b** adapted with permission from ref. <sup>119</sup>, copyright Elsevier 2015)

treatment was not favourable for improving the corrosion resistance of the SLMed Ti6Al4V alloy.

Other studies with the SLMed Ti-based alloys were also investigated, including Ti24Nb4Zr8Sn for biomedical applications,<sup>85,151–153</sup> Ti6.5Al3.5Mo1.5Zr0.3Si for aerospace applications,<sup>154,155</sup> and so on.

Al-based alloys

The SLM of the following aluminium alloys has been investigated: Al-Cu,<sup>156–158</sup> Al-Zn,<sup>159</sup> AlSi12,<sup>160–163</sup> AlSi50,<sup>164</sup> and AlSi10Mg,<sup>70,115,165–172</sup> with AlSi10Mg receiving the most attention.

The microstructure of the SLMed AlSi10Mg alloy was characterised as a fine cellular-dendritic pattern, and silicon was found

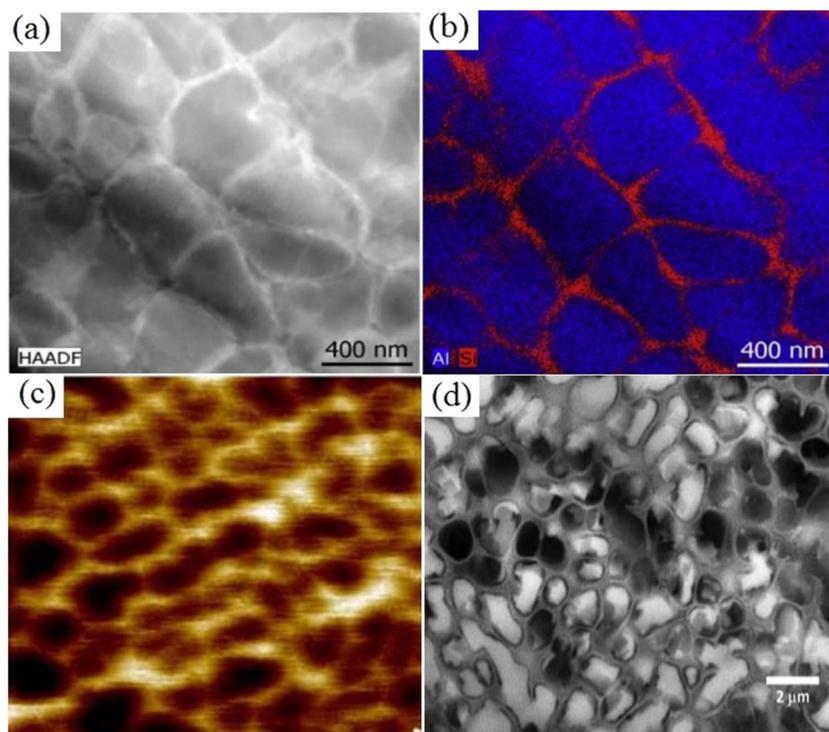
to be located primarily at the cellular boundaries, as displayed in Fig. 9.<sup>173–175</sup> The potential of the aluminium phase was lower than that of the silicon phase, leading to galvanic corrosion and Fig. 9d displays the intercellular network of silicon in the corroded areas for the SLMed AlSi10Mg alloy in chloride solution. Thus, post heat treatments were conducted on the SLMed AlSi10Mg alloy to homogenise its composition and improve the corrosion resistance.<sup>176,177</sup> However, the silicon in the SLMed 2024 aluminium alloy promoted  $\text{Al}_2\text{Cu}$  precipitation and hindered the  $\text{Al}_2\text{CuMg}$  phase, which led to a decreased uniform corrosion rate (5 times lower) compared to that for the commercial 2024 aluminium alloy in chloride solution. Moreover, a thicker aluminium oxide film was obtained on the SLMed 2024 aluminium alloy in comparison to that on the wrought counterpart.<sup>178</sup>

### Fe-based alloys

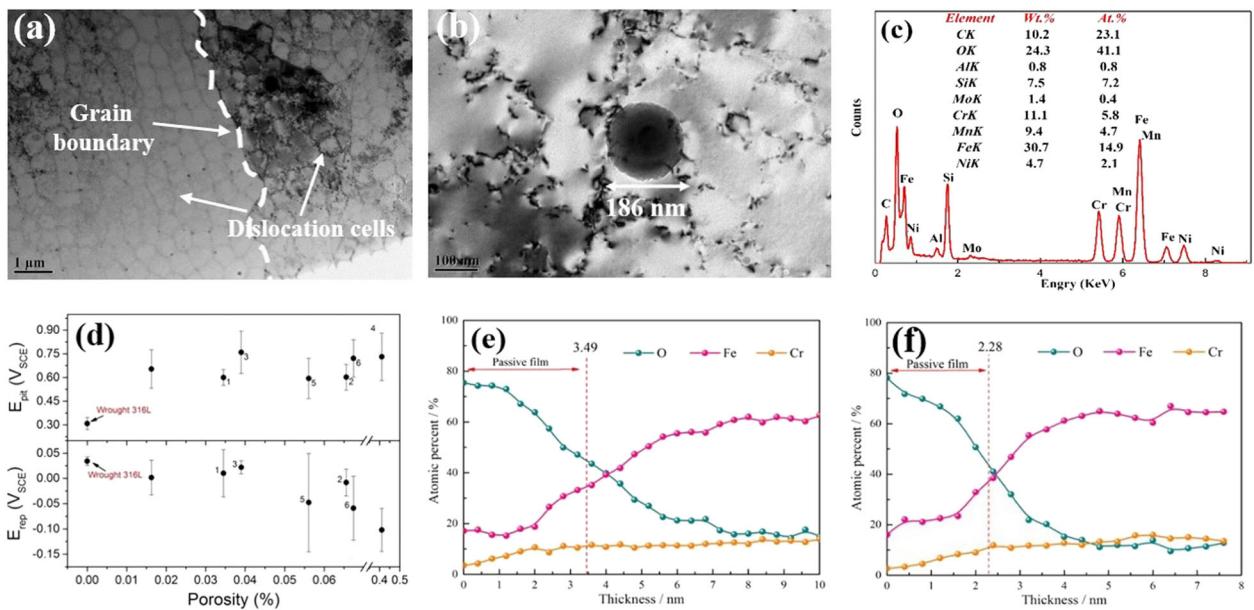
Austenitic stainless steels (such as 304L and 316L) can still exhibit a complete austenitic phase after SLM fabrication,<sup>37,179,180</sup> but the ferrite phase can be formed during laser melting deposition (with a slower cooling rate compared with SLM).<sup>8,181–183</sup> In the SLMed 316L stainless steel, there were many dislocation cells inside the grain, which led to a higher hardness and strength in comparison to the wrought counterpart.<sup>36,184–187</sup> Moreover, nanoscale inclusions (diameter ranging from 100 to 200 nm) were extensive in the SLMed 316L substrate and were enriched with Si, Al, Mn and O as displayed in Fig. 10b, c, which was also confirmed by other reports.<sup>50,188–190</sup> The oxide inclusions of this scale were not deleterious to the pitting corrosion resistance.<sup>191,192</sup> However, no MnS inclusions or large (Al, Ca)-oxide precipitates have yet been observed in the SLMed 316L stainless steel, which should be attributed to the extremely high solidification rate during the SLM process, however, there was enough time for the element diffusion (such as Mn and S) to form those inclusions during the traditional casting process.<sup>193,194</sup> Thus, a higher pitting potential

(~300 mV) was obtained for the SLMed 316L stainless steel compared to that of the wrought material in 3.5 wt.% chloride solution, as displayed in Fig. 10d, and the porosity of the SLMed 316L stainless steel in his work had no effect on the pitting potential (the porosities were all below 0.5%).<sup>69</sup>

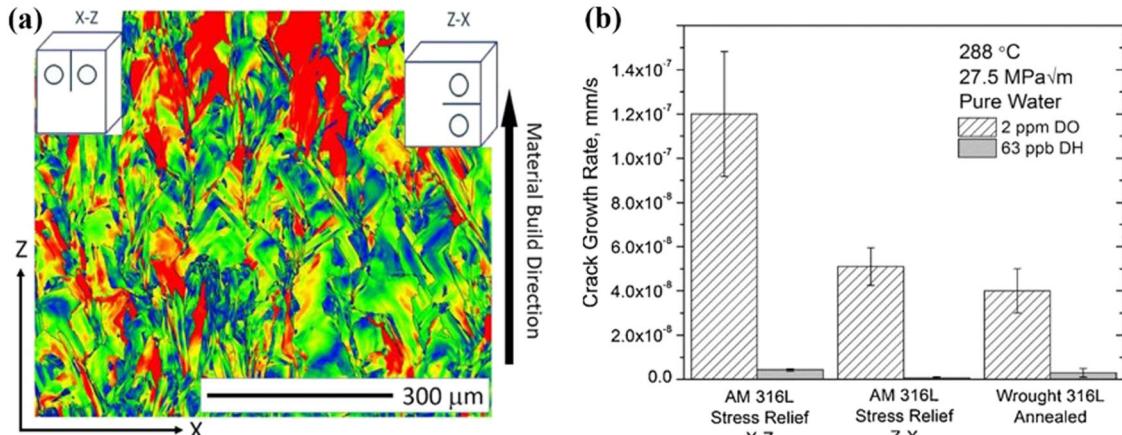
Meanwhile, Sander et al.<sup>69</sup> emphasised that there was a lower frequency of metastable pitting for the SLMed 316L specimens than that for the wrought in chloride solution. They also pointed out that the protective potential decreased with increasing porosity, which could be ascribed to the poor re-passivation ability at the pore sites. An Auger electron spectroscopy measurement confirmed that the passive film formed on the SLMed 316L stainless steel in simulated body fluid for 96 h was ~1.5 times thicker than the film formed on the wrought 316L stainless steel, as displayed in Fig. 10e, f. Similar results were also confirmed on the SLMed AA2024 aluminium alloys.<sup>177</sup> At the same time, oxidation reactions preferentially occurred at the high dislocations sites of the 304 stainless steel due to the high activation energy of localised lattice distortion,<sup>195</sup> which means that thicker passive film can be formed on the SLMed samples due to the high density of sub-grain boundaries. Stress corrosion cracking is usually detrimental for stainless steels, and the influence of the crack orientation was critical in evaluating the stress corrosion cracking property because the SLMed 316L stainless steel exhibited an anisotropic microstructure and complex geometry.<sup>121</sup> The SLMed 316L parts showed a higher crack growth rate along the building direction than the other two directions or the wrought material and the differences were more than a factor of two ( $1.2 \times 10^{-7}$  mm/s vs.  $5 \times 10^{-8}$  mm/s in 2 ppm dissolved oxygen) as displayed in Fig. 11. The crack growth rate of the SLMed 316L stainless steel perpendicular to the building orientation was similar to the wrought 316L stainless steel.<sup>196</sup> The slower crack growth perpendicular to the building orientation may be due to the difficulties the crack encountered when attempting to cut through the vertically oriented and closely spaced columnar



**Fig. 9** **a** STEM HAADF image of SLMed AlSi10Mg, **b** Al and Si X-ray map<sup>173</sup> and **c** the surface potential mapping results (Colour bar: 210 mV range) and **d** the corroded morphology in NaCl solution.<sup>207</sup> (**a** and **b** adapted with permission from ref. <sup>173</sup>, copyright Elsevier 2016) (**c** and **d** adapted with permission from *J. Electrochem. Soc.*, **164**, C27, 2017, copyright 2017. The Electrochemical Society)



**Fig. 10** Transmission electron microscopy images **a**, **b** and **c** the EDS results of the nano-inclusion of the SLMed 316L specimens,<sup>36,82</sup> **d**  $E_{\text{pit}}$  and  $E_{\text{rep}}$  values against the respective sample porosity in 3.5 wt.% chloride solution,<sup>69</sup> and passive film thickness on the **e** SLMed and **f** wrought 316L stainless steel after immersion in simulated body fluid for 96 h obtained by auger electron spectroscopy.<sup>37</sup> (a) adapted with permission from ref. <sup>36</sup>, copyright Elsevier 2018 (b and c) adapted with permission from ref. <sup>82</sup>, copyright Elsevier 2018 (d) adapted with permission from *J. Electrochem. Soc.*, **164**, C250, 2017, copyright 2017. The Electrochemical Society (e and f) adapted with permission from ref. <sup>37</sup>, copyright Elsevier 2018)



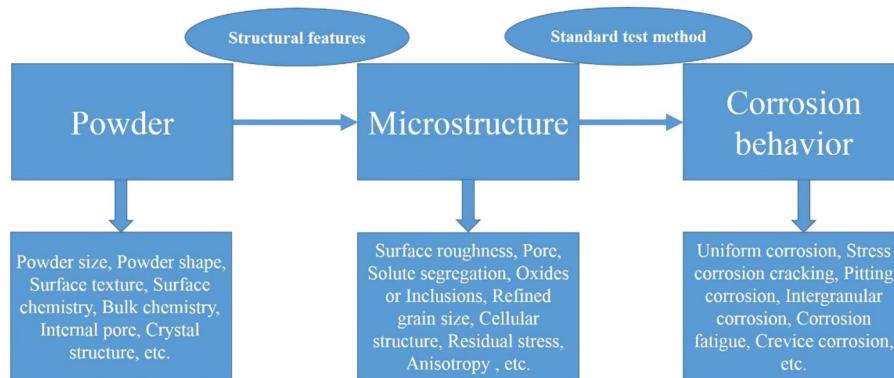
**Fig. 11** **a** EBSD map and **b** stress corrosion cracking growth rate of the SLMed (stress-relieved with no additional cold work) and wrought 316L stainless steel in normal (2 ppm dissolved oxygen) and hydrogen water chemistry environment (63 ppb dissolved hydrogen).<sup>196</sup> “X” refers to the direction perpendicular to the material building direction, and “Z” refers to the direction parallel to the material building direction. (a and b) adapted with permission from ref. <sup>196</sup>, copyright Elsevier 2018)

grains. The crack paths were more tortuous and encountered more grain boundaries than those propagating on the plane perpendicular to the building orientation.<sup>196,197</sup> The microstructural anisotropy can be eliminated after high-temperature recrystallisation annealing and the results revealed that the annealed SLMed 316L stainless steel showed a slower crack growth rate than the stress-relieved counterpart.<sup>128</sup> Thus, recrystallisation annealing heat treatment is necessary for the SLMed 316L stainless steel to improve its resistance against stress corrosion cracking.

## CONCLUSIONS AND FUTURE WORK

An overview of the current state of some metallic materials fabricated by SLM technology was presented with a focus on the

relationship between the internal microstructures and the related corrosion properties. A consensus was reached that a high-temperature gradient involved in the SLM process typically yields significant grain refinement and a high density of dislocations, leading to a notably high tensile strength. For corrosion resistance, it depends on whether or not phases or structures with poorer corrosion resistance are generated compared to the traditional processed counterparts. In the near future, the variety of AM materials is expected to increase, and the optimisation of the fabrication parameters to obtain a high strength, low surface roughness and minimal porosity will always be the focus. However, the internal relationship between the microstructural features and the corrosion behaviour of the printed parts should also be studied systematically. Research should begin with the



**Fig. 12** Schematic diagram involving the powder, microstructure and the related corrosion behaviour for AM-produced components

input powder material properties and their effects on the building process. When characterising a powder, it is important that the following three main parts are included: particle morphology, particle chemistry and particle microstructure.<sup>198–201</sup> Currently, research is primarily focused on the morphological characterisation of powders and their effect on the properties of fabricated parts. The properties of the final consolidated components, such as the mechanical and anti-corrosive properties, may also be influenced by whether the feedstock powders are argon- or nitrogen-atomised and whether the build chambers are argon- or nitrogen-purged.<sup>202–205</sup>

Figure 12 shows a schematic diagram involving the powder, microstructure and related corrosion behaviour of AM-produced components. It is necessary to establish the relationship between the key structural features and corrosion resistance. For example, typical MnS inclusions formed in wrought 316L stainless steel were substituted by nano sized Mn-Si oxides in the SLMed counterparts, reducing the pitting susceptibility,<sup>36,188</sup> and microstructural anisotropy for the SLMed parts led to different SCC growth rates.<sup>196</sup> For the corrosion testing methods, there is an obvious lack of standards for which baseline or standardised tests are executed, and up to now, a broad range of different corrosion test methods (such as corrosion potential, polarisation, impedance spectroscopy, weight-loss experiment, etc.), make cross comparisons difficult. The acceptance of standardised testing procedures formulated by professional bodies, such as the ASTM in the United States, is one approach to solve this problem.

In general, the defects in the SLMed parts (such as pores and MPBs) usually comprise the corrosion resistance, therefore, a heat treatment combining the hot isostatic pressing should be considered to homogenise the composition and microstructure, and reduce the porosity. Another post-processing method involves surface treatment, but surface treatment has been an ongoing challenge with the SLMed metals from the initiation of this technology. Surface modification techniques, including sand blasting, electrochemical deposition, alkali-acid-heat treatment, electrochemical etching and micro-arc oxidation, can be chosen according to the characteristics of the material. However, surface modification of printed porous metals is more challenging than that of solid implants because of the compatibility with widely used line-of-sight techniques; thus, the choice of available methods is very limited. Therefore, further research in this area is also warranted.

## ACKNOWLEDGEMENTS

This work was supported by the National Key Research and Development Programme of China (No. 2017YFB 0702300), Fundamental Research Funds for the Central Universities (No. FRF-TP-17-002B), National Natural Science Foundation of China (No.51671029).

## AUTHOR CONTRIBUTIONS

D.K., X.N. and C.D. reviewed and analysed the literature on the corrosion of selective laser melted alloys. D.K. and C.D. wrote the paper. C.D. and X.L. reviewed and modified the paper and final approval of the version to be published was given by all authors.

## ADDITIONAL INFORMATION

**Competing interests:** The authors declare no competing interests.

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