

Review

# A Review on Mechanical and Corrosion Behaviour of DMLS Materials

## A. P. S. V. R. Subrahmanyam<sup>1\*</sup>, K. Siva Prasad<sup>2</sup>, P. Srinivasa Rao<sup>1</sup>

<sup>1</sup>Centurion University of Technology & Management, India <sup>2</sup>Anil Neerukonda institute of Technology and Sciences, India E-mail: subbuaynavilly@gmail.com

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**Abstract:** Direct Metal Laser Sintering (DMLS) is an Additive Manufacturing (AM) technique in which the metal powder will be sintered in selected regions as per 3D Computer-Aided Design (CAD) file in stack manner to produce a three-dimensional object with less effort, in less possible time, and with minimal wastage of metal. In this paper, most widely used DMLS metal powders mechanical and corrosion properties are analyzed, and the effects of post processes on the material properties are discussed. The objective of the paper is to consolidate previous research efforts and to identify gaps to identify the key areas of this technology. The promising and successful application of this revolutionary technology in various sectors like biomedical, aerospace, and automotive was also discussed based on material behaviour at different operating conditions. This review would help researchers to find challenges in this booming technology. As per the materials point of view, future research prospective was suggested in depth in light of present review.

*Keywords*: Direct Metal Laser Sintering (DMLS), additive manufacturing, metal powders, mechanical properties, corrosion properties

#### 1. Introduction

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At present, Additive Manufacturing (AM) is an invigorated technology in sectors like bio medical, dentistry, aerospace, automobile and manufacturing [1]. In this technique, there is an addition of material in a stacking manner to build a prototype or a functional part despite of subtracting material from stock as in the case of conventional machining. Beside of having limited availability of feasible materials and machines, it is emerging technology capable of producing small and medium lot size parts in relatively less time with more accuracy. There is availability of more work space and flexibility of manufacturing due to no tooling. According to ASTM F42, the AM technologies are of two types namely Material Extrusion, Material Jetting, Powder Bed Fusion (PBF), Binder Jetting, Sheet Lamination, VAT Photo Polymerisation and Direct Energy Deposition (DED).

In the present paper we emphasized only on Direct Metal Laser Sintering (DMLS), one of the techniques of PBF. In DMLS metal powders are used to build a 3D object directly from a 3D CAD file. Basically, the final object can be obtained in the machine on a moveable platform by applying powder material as successive layers [2]. After a layer was spread by recoater blade, a high power laser beam is directed on to powder bed and it will sinter the powder particles at desired locations as per given 3D file. The platform moves down the pre programmed layer thickness, a fresh film of powder is spread and the next layer is melted with exposure to the laser source, so that it conforms to the previous layer.

This process continues, layer by layer, until the object is fabricated. This process was depicted in Figure 1.

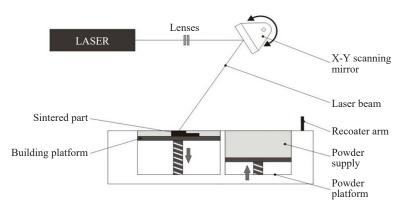


Figure 1. Schematic representation of DMLS process [3]

Selective Laser Melting (SLM) machines are also called as DMLS machines [4], [5]. In this paper SLM also referred as DMLS. Various European countries produce machines with beds that are able to do laser sintering and laser melting [6]. It is a design driven wide spread process because of the availability of different metal powders with desired size, shape and weldability. In this technology it is desirable to have metal powders in the form of spherical and nearly spherical geometry and in tens of micron size to achieve good bonding, homogeneity and crack free products [7]. Among the 50 different atomized powders within reach, most widely used metal powders in AM technology are Tibased alloys, Nickel based super alloys, Al based alloys, Co-Cr alloys, Stainless steels (316L and 17-4PH), Precious metals (Au, Ag), Refractory metals (W, Ta), Cu based alloys, intermetallic and low alloy steels [8]. In DMLS process a porous internal structure can be used to lessen the weight and assuring the strength at the same time. This results in considerable redeeming in powder material and weight as well as energy consumption during processing [9]. This feature of DMLS will attract the automobile sector where there is a continuous research to reduce weight, improve strength and functionality [10].

The main intent of this paper is to analyze studies that were conducted earlier on DMLS Ti-6Al-4V, AlSi10Mg, Stainless Steels, Nickel based super alloys and Co-Cr alloys. The mechanical, tribological and corrosion properties of each of these materials was discussed in detail in the sections 2. The identified gaps and future concerns were given in conclusions part.

### 2. Literature review

In this section the effect of process parameters and post processes on the performance of DMLS materials reported earlier was discussed ornately.

#### 2.1 Characteristics of Ti-6Al-4V

The Ti-6Al-4V alloy is widely used in DMLS process because of its copious applications in biomedical, aerospace, marine and offshore applications. They have good fracture toughness, fatigue behaviour, corrosion resistance and biostability [11], [12]. DMLS technology helped automakers to produce parts of high quality, cost effective, robust and consistent parts [13], which could be a best alternate to traditional manufacturing processes. Since porous structured parts with desirable strength can be produced. Materials produced by DMLS comprehend few defects that have an effect on their mechanical properties. Various research works conducted to find the effect of input parameters on the defect engenderment in DMLS process. The DMLS product quality depends upon factors like laser power, laser scan speed, hatch distance, laser energy density and layer thickness.

The as built DMLS specimens are prone to cracks due to porosity defects. Porosity defect can form due to meagre

energy input or due to the use of extravagant energy [14]. So even if the crack initiated was observed to have incessantly started on the surface, the pores network can act as a barrier for the crack proliferation and cause the sample breakdown. Figure 2 shows the defect observed at fractured surface which is irregular in shape and these types of defects are occurred particularly due to fusion paucity and variable particle sizes of powder [15]. The possible sources for defect generation are unmelted or partially melted powders particles causing inadequate fusion, delamination between successive passes or earlier deposited layers and inducement of gases during manufacturing.

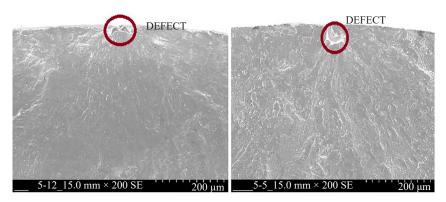


Figure 2. Fatigue fracture origins of surface polished DMLS specimens [14]

Excessive or much low energy input lead to emergence of different defect generation mechanisms [16]. The hatch distance and scan speed have an impact on surface hardness and final density [17]. Decrease in laser speed and hatch distance lead to increased hardness [8]. Brazinova et al. [18] studied the effect of laser power on the hardness of Ti-6Al-4V before and after annealing. It was revealed that the hardness and laser power are directly proportional for both perpendicular and parallel directions of the deposit layers before annealing and it was comparatively more in perpendicularly built specimen. After annealing hardness shown negative impact for all laser powers for both build directions due dissolving of material structure pattern. Figure 3 shows the directions with respect to build platform.

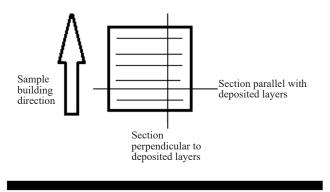


Figure 3. Specimen orientations with respect to build direction [18]

Anna Guzanova et al. [19] stated that isotropy in mechanical properties of DMLS component resulted due to stressrelief annealing; it considerably reduced the difference in hardness between the two directions (Parallel and perpendicular to build direction). DMLS products have inherent surface roughness, which will limit their applications in automotive and biomedical applications. The as-built surface roughness can be reduced by some surface machining processes. The inherent surface roughness is mainly due to improper process parameters and partly melted powder particles. The surface roughness has a great effect on fatigue life of DMLS Ti-6Al-4V.The surface roughness depends

on powder quality, AM system, Processing parameters and notch orientation. Surface machining improves considerably the fatigue strength of as-built Ti-6Al-4V product produced by DMLS [20]. Baca et al. [21] carried out a study on the effect of build orientation on fatigue strength of Ti-6Al-4V made of DMLS and found that the built direction had clear influence on fatigue performance and it was less in specimens built parallel to build direction.

Few authors tried to revamp the fatigue strength of DMLS Ti-6Al-4V by providing some post heat treatment processes. The Hot Isostatic Pressing (HIP) improves ductility of the DMLS Ti-6Al-4V samples due to the formation of  $\alpha + \beta$  microstructure and it doesn't have any effect on roughness since there is a limit in size and shape of internal pores [22]. The observed microscopic images were shown in Figure 4. Greitemeier et al. [23] suggested that in order to prevent influence of surface roughness on fatigue behaviour of DMLS component HIP was used since, it can minimize the internal defect size. The surface quality of DMLS Ti-6Al-4V can be improved by combining blasting and chemical etching. Blasting minimizes surface irregularities and etching makes surface clean [24].

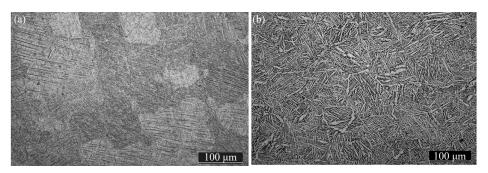


Figure 4. Microstructure of a) As-built b) HIPed DMLS samples [22]

Due to rapid cooling in DMLS process there is a change of micro structure from columnar  $\beta$  grains to  $\alpha$  martensite needle form through which the fatigue crack will grow [25]. As-built DMLS Ti-6Al-4V can be used for biomedical applications since after heat treatment at 680 °C for 3 hrs its tensile strength decreased from 1,265 MPa to 1,170 MPa, while ductility increased by 10.9% [26]. Moletsane et al. [27] concluded that the properties of DMLS specimens from Ti-6Al-4V (ELI) requires only stress-relieving and can meet required standards.

Ti-6Al-4V has excellent biocompatibility, and high corrosion resistance which have resulted in them being used in many engineering and biomedical applications. Ti alloy is widely used in prosthesis, dental restorations and space applications due to its excellent corrosion resistance [28]. A corrosive resistant oxide film mainly composed of TiO<sub>2</sub> naturally formed on its surface. The formation of quick and chemically stable protective layer formed on material surface can offer better resistance to corrosion [29]. Ti-6Al-4V a duplex structured one, with  $\alpha$  phase (hcp) and  $\beta$  phase (bcc). Ti-6Al-4V alloy exhibits a wide range of microstructures and is considered to be a heat treatable Ti alloy. When it is heat treated the chemical composition and  $\alpha$ ,  $\beta$  volumes will be altered and show variation in properties. Jhen-Rong et al. [30] from their study on corrosion behaviour of Ti-6Al-4V in 0.5 mol  $1^{-1}$  H<sub>2</sub>SO<sub>4</sub> + 1 mol  $1^{-1}$  HCl solution found that selective dissolution of  $\alpha$  phase was occurred when the potential was increased to -0.9 Vpt and galvanic corrosion was observed at the boundary of  $\alpha$  and  $\beta$  phases. From the microstructural analysis of the SLM Ti-6Al-4V, it was clearly evident that it contains high amount of  $\alpha$  phase and less amount of  $\beta$  phase, whereas grade 5 alloy contain  $\alpha + \beta$  phase in its microstructure. This was the reason for inferior corrosion resistance of SLM Ti alloy [31]. According to Longhitano et al. [32] the heat treatments combined with anodizing shown more impact in enhancing the corrosion and mechanical properties of Ti-6Al-4V. The anodizing process reduced the passive current density and heat treatment increased  $\beta$ phase. There was a difference in corrosion resistance offered by horizontally build and vertically build specimens due to difference in amount of  $\alpha$  and  $\beta$  phases in cross sectional and longitudinal direction, which shows that anisotropic nature of DMLS material will affect its corrosion resistance [33]. Żebrowski et al. [34] used surface treatment shot peening to improve surface quality of DMLS Ti-6Al-4V and reported that shot peening at low frequencies was found to be effective in reducing surface roughness and improved its corrosion resistance.

Based on the earlier works reported on DMLS Ti-6Al-4V, it is understood that DMLS component contains

inherent surface roughness and defects. Proper selection of process parameters plays a major role in the quality of final product. Maximum of works done on mechanical characterization of DMLS product based on process parameters. Post processing is required in order to enhance strength of DMLS product. It is revealed that surface finishing treatments and HIP process improves ductility and fatigue strength. Stress-relief annealing is also required to relief stresses formed during rapid cooling of DMLS product. The works done before on corrosion studies of DMLS Ti-6Al-4V made it clear that it has superior corrosion resistance than cast/ wrought counter parts.

Very few research works identified causes of defects and possible remedies. There is scope remained open to evaluate tribological characterization of DMLS Ti-6Al-4V product. Low cycle fatigue, fatigue crack growth, fracture toughness, impact, creep, creep fatigue, multi axial testing and environmental effects are needed to be explored more. The control of grain growth can possibly be addressed to study anisotropy and change of corrosion resistance between  $\alpha$  and  $\beta$  phases.

## 2.2 Characteristics of AlSi10Mg

Al-Si base alloys find wide applications due to its high strength to weight ratio, good corrosion and wear resistance. AlSi10Mg alloy can be used for high weight applications due to its high strength, hardness and good resistance to wear. AlSi10Mg is best suited for casting complex and thin walled parts. AlSi10Mg made parts are having the combined advantage of good thermal properties and low weight. Al alloy is mostly used in aerospace and automotive interior parts and few functional parts due to its high strength to weight ratio, good thermal conductivity and corrosion resistance [35]. Due to near eutectic composition of Al and Si they can be easily processed by laser application [36]. AlSi10Mg manufactured by DMLS and the effect of process parameters on its properties were studied. The brief review of works reported on DMLS AlSi10Mg was listed here.

Manickavasagam et al. [37] identified that hatching distance and scanning speed showed a much influence on mechanical properties of DMLS AlSi10Mg. The gas entrapment will be increased due to increase in hatch distance which consequently reduces melt pools overlapping. Reducing the scanning speed increases the Linear Energy Density (LED). Among various process parameters, laser power and hatch distance have more influence on ultimate tensile strength [6]. Wang et al. [38] explored the impact of LED on the surface quality of As-built AlSi10Mg and concluded that the surface quality was improved by increasing LED. The effect of process parameters was studied by Calignano et al. [39] and identified that scan speed has a great influence on surface roughness and shot peening significantly reduced surface roughness as they observed through SEM analysis and were shown in Figure 5. Proper amalgamation of scanning speed and laser power can give better surface finish to DMLS products [40]. The powder characterization is also an important factor for DMLS AlSi10Mg. Very fine size powder particles shows negative impact on mechanical properties. Particles less than 10 micron size agglomerate and forms clusters which will avoid flowability and finally causes porosity. Manfredi et al. [41] used AlSi10Mg powder particles of spherical shape size ranging from 21 to 27 microns and stated that the ultimate tensile strength, yield strength and elongation at break were improved as compared to cast Al360 alloy.

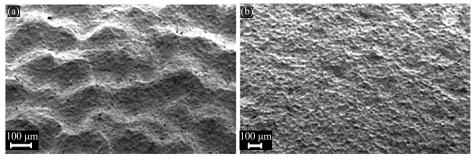


Figure 5. Surface of samples a) before and b) after shot peening [39]

The parts made by DMLS AlSi10Mg have problem of porosity and surface roughness. The surface quality of

DMLS AlSi10Mg had a great influence on its fatigue strength. The As-built DMLS component has inferior fatigue strength when compared to conventional part due to porosity and surface cracks [42]. The Al Metal matrix composites reinforced with Silicon Carbide particulates (SiCp) of different mesh sizes and volume fractions were prepared by Ghosh et al. [43] through DMLS route. They found that with increase in volume percentage of SiCp the Crack density increased and the specific wear rate increased with decrease in mesh size. The small size SiCp increased porosity. The porosity defect was depicted in Figure 6. The reason was coarser grain size lead to gap formation between grains.

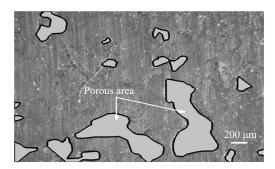


Figure 6. Example photograph showing typical porous area [43]

Optimized combination of process parameters and surface finish can improve the fatigue strength [44]. The fatigue behavior enhancement was always difficult due to defects that remained even after surface polishing. The fatigue crack formation is a major problem in DMLS AlSi10Mg. The sudden cooling of DMLS component from high temperature will create temperature gradient which will induce residual stresses. Heat treatment will make the DMLS component isotropic. Raising the platform temperature will also reduce formation of residual stresses and there by crack propagation [45].

Lorusso et al. [46] studied the tribological behaviour of AlSi10Mg-TiB<sub>2</sub> composite made by DMLS process. They found that DMLS AlSi10Mg-TiB<sub>2</sub> Metal Matrix Composite (MMC) showed less wear than casted AlSi10Mg-TiB<sub>2</sub> Composite. They further suggested that addition of nano sized reinforcements gives better wear properties. The wear rate comparison was shown in Figure 7. Majeed et al. [47] acknowledged that solution heat treatment process reduced the average surface roughness by 17% at 540 °C for 2 hours. Sand blasting (post treatment) has a positive effect on DMLS component that reduced average surface roughness by uniform distribution of porosities in the cross section and created superficial compression state in material that improved fatigue resistance [48], [49].

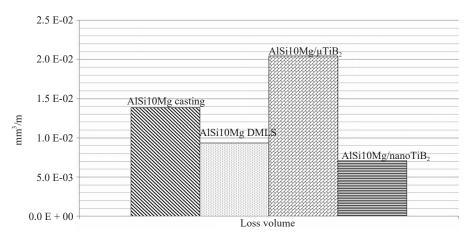


Figure 7. Volume per meter loss after wear tests of the AlSi10Mg samples obtained by casting and DMLS, and of the composites with micro- and nanoTiB<sub>2</sub> particles [46]

Due to ever increasing demand in marine and automotive sectors, the additive manufacturing finding its own way of exploring new materials to suit these environments. Among those suitable candidate materials Aluminium alloy (AlSi10Mg) is most preferable one due to its qualities like high strength, light weight and good corrosion resistance. It shows corrosion resistance due to the formation of passive protective film. This passive film acts as a barrier for transfer of ions [50].

Yucheng et al. [51] from their simulation studies concluded that increase in laser power increased corrosion resistance of SLM AlSi10Mg. During laser sintering there was segregation of Si particles and during rapid cooling there was a precipitation. The corrosion characteristics mainly depend on the type of elements present in alloy and the potential difference between them. The potential difference between Al and Si caused galvanic corrosion. The potential difference between Al and Si was higher at melt pool boundaries, which would be the most attacked region of corrosion. The cracks formed due to residual thermal stresses during rapid cooling would also promote corrosion. This can be arrested by increasing the build platform temperature. Raising the build platform temperature up to 100 °C reduces internal stresses without affecting the mechanical and corrosion resistance of DMLS AlSi10Mg [52].

The stress reliving post heat treatment at 200-300 °C caused precipitation of Si in microstructure and increased selective corrosion attack. The T6 heat treatment and Stress relief heat treatments resulted in Si particles coarsening and lead to microstructural change. The T6 heat treatment destroyed the existed microstructure of as-built SLM Al alloy which further affected its mechanical and corrosion properties [53]. The as-built specimen was more sensitive to intergranular corrosion after 24 hrs of immersion time [54]. Girelli et al. [55] investigated the corrosion behaviour of DMLS AlSi10Mg and Gravity Casted (GC) AlSi10Mg. The as-built DMLS specimen showed superior corrosion resistance than casted counterpart. T6 heat treatment has shown advantage for DMLS alloy in immersion in chloride-bearing environment but it was not effective for casted specimen. The corrosion behaviour of AM Al alloy was better than die casted part in both asbuilt and T6 heat treatment conditions [56]. This can be seen from Figure 8.

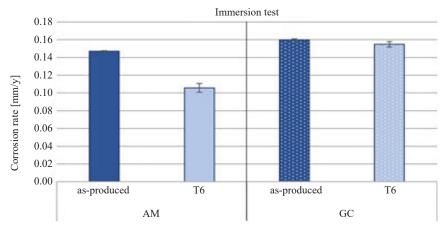


Figure 8. Corrosion rate of DMLS and GC specimens after 28 days of immersion [56]

The work done so far on DMLS AlSi10Mg given limited information regarding its mechanical properties. The selection of laser scan speed and power will show a considerable effect on porosity and surface roughness. Some authors came up with possible ways to reduce porosity and surface roughness. Shot peening and solution heat treatment showed a possible impact in decreasing surface roughness and there by fatigue strength. Large number of studies was done on mechanical characterization of DMLS component based on input parameters. It was evident that the corrosion resistance of DMLS AlSi10Mg was better than that obtained by conventional method like casting. This was due to its fine microstructure containing Si particles surrounding eutectic Al particles. Heat treatment at higher temperatures deteriorated the corrosion resistance of DMLS specimen. To heat treatment decreased corrosion rate of DMLS specimen. The surface quality plays a vital role in its corrosion resistance. The grounded DMLS specimen has shown better corrosion resistance due to the formation of strong passive film on its surface. The cracks that will initiate due to thermal residual stresses of rapid cooling can be reduced by increasing build platform temperature.

Limited research was addressed on the characterization of DMLS AlSi10Mg product using powder particles size, build orientation and post processing methods. These areas need to be work more. Addition of nano reinforcements in the fabrication of DMLS composites could be a new research area. For better quality of DMLS AlSi10Mg, concern remained open to explore more about process parameters and post or pre treatments to overcome problems listed above.

#### 2.3 Characteristics of stainless steels

The stainless steel materials used in DMLS method were SS316 Land PH1 steels. Stainless Steel PH1 is a prealloyed stainless steel in fine powder form. They have good corrosion resistance and high ductility which makes it a suitable material for biomedical and aerospace. These steels can be moulded into different shapes for different purposes by utilizing the maximum potential of this DMLS technology [57].

Though number of infiltration techniques was suggested for DMLS process, Porosity is still a problem [58]. So, proper combination of processes parameters must be used to reduce defects that normally present in DMLS steels. Antony et al. [59] carried out an experiment to understand laser power, scan speed and beam size influence on geometry characteristic and balling effect. They confirmed that laser power and scan speed have noticeable effect on distortion and irregularities. The mechanical properties can be improved by heat treating, changing energy density and combination of input parameters. The post heat treatment also increased the tensile strength in Stainless steel PH1 [60]. This was shown in Figure 9.

Mohamed et al. [61] found that horizontal specimens showed better density and mechanical properties than 45° oriented specimens in the case of 17-4PH Stainless Steel.

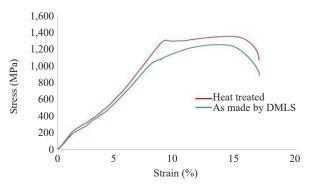


Figure 9. Stress-strain curve of DMLS steel before and after heat treatment [60]

Dario et al. [62] studied the effect of built orientation and thickness on the fatigue behaviour of DMLS SS 15-5PH and they concluded that the component built in slant position (45° to build orientation) shown reducing notch effect due to less scan errors. By removing the surface irregularities, residual stresses present at surface can be curtail and may lead to increase of the fatigue strength. Shot peening significantly stored high-magnitude compressive residual stresses on component surface which will improve the fatigue fracture resistance of DMLS component [63]. Alafaghani et al. [64] conducted mechanical testing at elevated temperature up to 350 °C heat treatment and concluded that 15-5PH can be used in different elevated temperature applications as there was no observable change in their micro structure but there is expected reduction in the tensile mechanical properties. The reduction of mechanical properties with temperature was shown in Figure 10.

Stainless Steel 316L is having high corrosion resistance and it can be used at temperature range below cryogenic temperature. It's kind of austenitic stainless steel commonly used in food processing, medical and aerospace applications. According to Bandyopadhyay et al. [65] the DMLS SS 316L is harder than commercial stainless steel. The laser power is responsible for the quality of product in DMLS. So, the process parameters need to be controlled effectively. It was found that better densification can be achieved with high laser power and low scan rate and less layer thickness and line spacing. In addition to these process parameters the powder properties also showed significant effect on mechanical properties of DMLS Stainless steel.

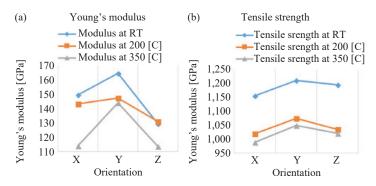


Figure 10. Mechanical properties of 15-5PH vs orientation at different environmental temperatures [64]

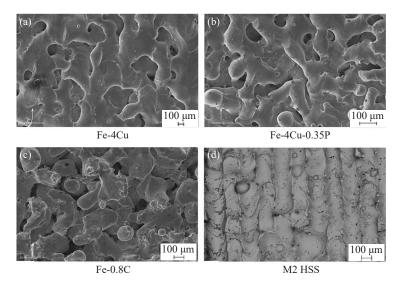


Figure 11. Example SEM images of different laser sintered steels [66]

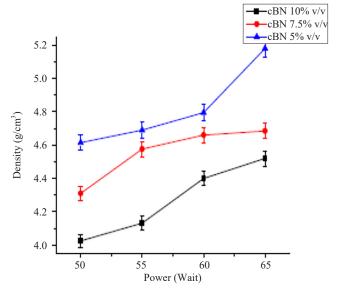


Figure 12. Effect of laser power on density [67]

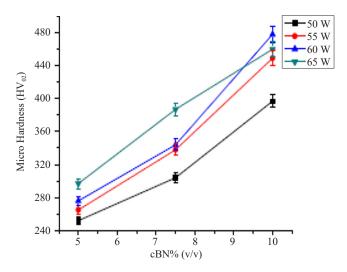


Figure 13. Effect of CBN on the micro hardness [67]

Powder chemical composition, particle size and shape show a clear impact on the DMLS product quality. Fine powder particles will increase exposed surface area, which will absorb more laser power, thereby increasing sintering area. Higher laser power will vaporize the metal powder, which is uneconomical. Not only powder properties the laser sintering pattern and laser sintering atmosphere will show a clear influence on densification of product. The delamination problem happens mainly due to thermal gradients present in the material. Figure 11 shows that delamination in different steels at high laser power. The same was reported by Simchi [66]. Hussain et al. [67] fabricated a MMC through DMLS route using SS316L matrix and CBN reinforcement in nitrogen atmosphere. There was a good compatibility between SS316L and CBN. With increase in laser power the relative density of the sintered samples was increased as shown in Figure 12. Increase in CBN content the micro hardness and wear resistance increased but it showed negative impact on relative density as represented in Figure 13.

Vijay et al. [68] fabricated TiN reinforced SS316 Metal Matrix Composite (MMC) and they observed that laser power showed a negative effect on part density and positive effect in reducing porosity up to certain level. With increase in TiN reinforcement the micro hardness of composite was improved. But, further increase in reinforcement after 20% volume increased wear rate due reduction in bonding between matrix and reinforcement. The previous work on stainless steel concentrated mainly on the influence of process parameters like laser power, scan speed and built orientation on its properties like tensile strength, micro hardness, surface roughness fatigue strength and wear rate. Some works stated that post heat treatment processes improved mechanical properties. There was a good compatibility of reinforcements in steels which improved its wear resistance.

Corrosion of austenitic steels can be classified as general and localized. General corrosion of austenitic stainless steel happens in mineral acids such as hydrochloric, sulphuric and nitric acids. AISI 300 series austenitic steels are corroded by hydrochloric acid solutions. Such attack is due to aqueous HCl dissociation yielding chloride ions, that attack the passive film formed on the steel. Stainless steels belong 300 series subjected to mainly two types of corrosions attacks they are generalized corrosion and localized corrosion. The general corrosion normally happens in mineral acids like hydrochloric, sulphuric and nitric acids, which will deploy the passive film formed on steel surface. The localized corrosion arises due to micro voids on its surface which increases corrosion on those specific regions. The localized corrosion resulted in pitting and intergranular corrosion. Most of previous studies reported that chloride environmental show detrimental effect on corrosion behaviour of steels. The DMLS 316L subjected to pitting corrosion due to voids and porosity that normally produced due to sintering process itself. Chemical segregation at boundaries could also promote this. Heat treatment reduced the microstructural defects and consequently changed the corrosion pattern and morphology of pits formed [69]. The pitting corrosion was due to large interfacial stress and micro voids at melt pool boundaries [70]. The SLM 316L shown more crack growth rate in building direction, which resulted due to pits formed on its surface [71]. According to Sander et al. [72] the pitting frequency of SLM 316L was lesser than wrought material in chloride solution and passive film formed on SLM specimen is ~1.5 times thicker than that formed on wrought

material. The work done by Gennen et al. [73] confirmed that the HIP process in SLM 316L increased vulnerability of corrosion due to combining of residual cracks and consequently increasing nucleation sites of corrosion. Stainless steel 17-4 PH is precipitation hardening steel containing 3.5% copper in it. Solution heat treatment followed by aging created soft martensitic microstructure with microscopic Cu rich phase. Corrosion resistance of precipitation hardening steels mainly depends on chemical composition. The aging heat treatment increased the susceptibility of corrosion cracking [74]. The DMLS 17-4 PH subjected to pitting corrosion in chloride environment [75]. The formation of ferrous sulphate salts would play a key role in creation of passive protective film in case of steels. 17-4 PH steel shown better corrosion resistance in 0.5 M H<sub>2</sub>SO<sub>4</sub> when solution heat treated at 1,040 °C and subsequent aging at temperature 480 °C [76].

Olugbade et al. [77]-[80] developed a new method of creating nano structured passive oxide film on surface of steels using Surface Mechanical Attrition Treatment (SMAT). They successfully applied this method on the surfaces of SS 316L, 301 and 17-4 PH and found that SMAT was effective in increasing corrosion resistance of these steels. Thanks to Olugbade et al. for their efforts in exploring the possibility of improving the corrosion resistance of stainless steels and further studies need to conduct the adaptability of this SMAT to AM steels.

DMLS steels are showing positive trend after some heat treatments so there is a need to study their effects on micro structure and correlating them with observed properties. Limited work reported on characterization of DMLS steels based on powders size, shape and densification effect. DMLS Steels still need more attention on their corrosion performance and related mechanisms. The microstructural changes have profound effect on their corrosion behaviour. No general conclusions can be drawn according to literature that reported earlier. Limited work required done on the effect of surface treatments on corrosion behaviour of steels. The possibility of mixing different nano reinforcements and their effects on DMLS steels need to be studied.

## 2.4 Characteristics of Ni-based super alloys

The Ni based alloys were developed rigorously in the 20th century, because of their use in jet propulsion, aerospace and more. The Nickel based alloys used in DMLS manufacturing process are Maraging steels, Inconel 625, Inconel 718 and Hastelloy X. These Ni based alloys find wide applications in aerospace and turbo machinery, where there is a need of having low thermal conductivity and good corrosion resistance. Moreover, they are not prone to age hardening and they have high creep life. They not only work well at high temperatures but they can work better even at low temperatures. This is the reason why these Ni based alloys used in cryogenic applications. The turbine engine components can be precisely obtained by DMLS process, because it can produce the quality component with ease [81]. Apparao et al. [82] fabricated DMLS maraging steel and tested mechanical properties and found that hardness and tensile strength were improved by heat treatment which resulted in precipitated-phase strengthening. Monkova et al. [83] declared that maraging steels mechanical properties were influenced by heat treatment and orientation. The heat treatment effect on conventional and 3D printed steels was shown in Figure 14.

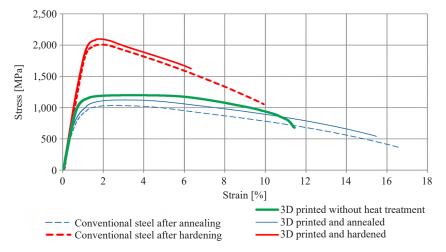


Figure 14. Strain-strain diagram of maraging steel for different heat treatments [83]

Jagadish and Priyanka [84] tested the effect of cryogenic treatment and build orientation on DMLS Maraging steel grade 300 mechanical properties. They confirmed that precipitation hardening improved mechanical properties. The cryogenic and aging processes improved the tensile and hardness properties. There was no significant difference in properties of horizontally built specimens and vertically built specimen. The diagrammatic representation was given in Figure 15.

Hadadzadeh et al. [85] used new class of maraging steel known as corrax steel in DMLS process and it contains fine microstructure with an average particle size of  $5.2 \pm 1.5 \mu m$ . These grains were equiaxed and decorated with austenite. So, it can be expected to be best choice for high strength applications. Schmidova et al. [86] found that DMLS maraging steel contains fine micro structure when compared to forging or casting and which is responsible for high dynamic and static strength. It was found that aging heat-treatment reduced Plastic anisotropy levels to a greater extent, however, transverse strain anisotropy was likely to remain due to the AM alloy's fabrication history [87].

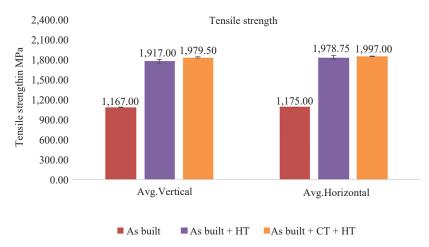


Figure 15. Effect of thermal treatments on Tensile strength [84]

The mechanical properties were found to be relying on process parameters and build orientation. The AM parts have some structural and surface defects, which will affect their wear and fatigue behavior. So, there is a need to carry out some post treatments/processes to overcome these defects. Kuo et al. [88] studied the creep properties of DMLS Ni-base superalloy with respect to build direction and heat treatment and concluded that the vertical (perpendicular to build direction) specimens showed higher values of creep life and ductility than horizontal built specimens, because of the interdendritic  $\delta$ -phase precipitates. The materials creep life and ductility was found to be effected by a row of interdendritic  $\delta$ -phase with incoherent interfaces. The Dendrite growth is as shown in Figure 16.

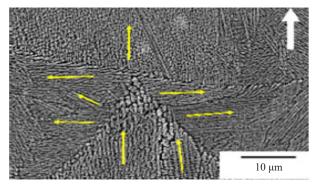


Figure 16. Molten pool boundary with dendrite growth [88]

Kelley et al. [89] studied the effect of parameters and build orientation on the properties of DMLS Inconel 718. There was an improvement of surface finish by post processing (micro machining). The fatigue strength in build orientation in Z is approximately 14% lesser than X/Y axes. The tensile and yield strengths were found to be 10% less in Z direction than X direction. Onome Scott et al. [90] concluded that Nickel alloy 718 was sensitive to DMLS process parameters and post processes like heat treatment and hot isostatic pressing. Components with fine grains were much harder than coarse grains. They found that vertically built specimens showed high tensile strength than horizontal built specimens. They used Ritz method to predict elastic modulus of DMLS Nickel alloy 718 plate and they suggested some alternative methods that might give good measurement of elastic modulus. The DMLS components made of Nickel based powders found wide range of applications in automobile and aerospace sector. So there is a necessity of concentration over its wear and surface roughness. Due to unavoidable surface roughness, the wear rate in DMLS components was relatively higher, the post treatments and optimized input parameters can improve the performance of these additive manufactured parts.

Naiju et al. [91] did research work on wear behaviour of Automobile self-starter center bush and front bush made up of bronze-nickel powder and they found that the wear rate of DMLS component is relatively higher than conventional manufactured bush, but they fall within the acceptable limits. From this, one can improve process performance by developing appropriate processing strategies in order to reduce defects normally arise in AM process. According to Solakolu et al. [92] the surface texture of DMLS component can be improved by reducing scanning speed and hatch distance. Surface quality is the main drawback that limits the acceptance of DMLS parts since it can show adverse effect on its properties. Various post processes and heat treatments were tried to improve the surface quality as well as mechanical properties of DMLS Ni alloy based components. Tan and Yeo [93] were studied surface quality of DMLS Inconel 625 after Ultrasonic Cavitation Abrasive Finishing (UCAF). They concluded that UCAF process improved surface quality of as built Inconel 625 significantly and it is shown in Figure 17. This process had removed surface irregularities efficiently without much altering of the DMLS part surface.

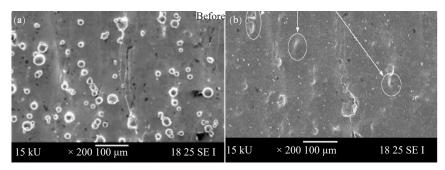


Figure 17. Surface topography of specimen a) before and b) after UCAF [93]

The ascendancy of different process parameters like scan speed, laser scan rate, laser power and hatch distance on micro hardness, final part density, dimensional accuracy and roughness was studied. With increase in laser speed there was increase in micro hardness and decrease in part density of DMLS Inconel 625. They also mentioned that decrease in hatch spacing (0.3 mm and 0.4 mm) will decrease micro hardness because of the formation of coarse grains due to low cooling rate [94].

Seetharaman and Krishnan [95] reviewed additive manufactured (DMLS process) Ni based alloys and concluded that the properties of DMLS Ni alloy was greatly influenced by input process parameters and post processes. Powder characterization, thermal conductivity and chemical composition were also important factors while manufacturing through DMLS route. The properties of additive manufactured parts showed better or equal mechanical properties compared to conventional manufactured parts. The influence of powder properties on product quality is shown in Figure 18. There is a need to use DMLS route to manufacture Inconel 718 than conventional manufacturing processes to save material being it is costlier. DMLS process also offers quick and easy method. Ni based alloys can be used in situations where the there is a need of high thermal resistivity and corrosion resistance.

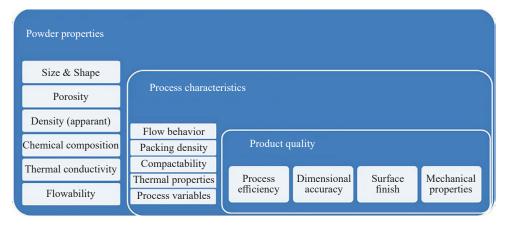


Figure 18. Part quality and process characteristics based on powder properties [95]

Scott et al. [96] tested the possibility of using DMLS Ni alloy 718 to manufacture hot section components like turbine blade and heat exchangers and compared tensile and fatigue properties of DMLS component with cold rolled Ni. Tensile properties were observed to be comparatively high for DMLS Ni alloy 718 mainly in transverse build direction. For high temperature and corrosion resistance applications like gas turbine blades, air craft engines and for process in which usage of chemicals there is a need of such alloy known as Hastelloy X. It is a Ni-Cr-Fe-Mo alloy. Wrought Hastelloy X exhibits a high tensile strength of 800 MPa and a percent elongation of approximately 50% at room temperature [97]. Hastelloy X can be used for the flame tube and casing of the combustion chamber due to its high creep strength and corrosion and oxidation resistance [98]. The alloy has nickel-based austenitic structure, called gamma ( $\gamma$ ) that can be strengthened by the addition of alloying elements [99]. While the addition of molybdenum and iron increases the strength, Hastelloy X is primarily used for its high corrosion resistance, because of its chromium content [100]. Chromium improves the oxidation resistance because it forms a protective  $Cr_2O_3$  oxide layer on the surface. This oxide layer is specifically known for its hot corrosion resistance.

There is a problem in using Hastelloy X through DMLS route because of the formation of micro cracks resulted from porosity and residual stresses. So there is a compromise in its mechanical properties. The methods like Solid solution strengthening, addition of carbides, heat treatments, hot isostatic pressing were improved its mechanical properties. Abbaschian et al. [101] altered the composition of Hastelloy X by adding Molybdenum to increase its solid solution strength thereby decreasing the crack density and marked an improvement of mechanical properties.

Ni super alloys can be used in severe operating conditions due to its excellent corrosion resistance, high temperature resistance and ability to withstand at high stresses. These Ni super alloys form a thin oxide layer on its surface which separates its surface from aqueous solution but tribological contact will deteriorate this thin film and will cause pitting attack and stress corrosion cracking [102]. The Ni super alloys find wide application in oil and gas industry where there is a need of material that can resist Sulphide Stress Corrosion Cracking (SSCC). Inconel 625 has high resistance to pitting and high Ni content make this more protected to chloride stress corrosion. Selective corrosion behaviour of SLM Inconel 625 was studied by Cabrini et al. [103] and they found that there was less penetration of acid attack for SLM 625 compared to hotworked, heat treated wrought alloy (Grade 1 625). The mass loss was also less for SLM product. They further reported that heat treatment at 980 °C followed by quenching prevented depth of penetration of selective attack. Inconel 718 used widely to make turbine blades due to its ability to withstand at high temperature and high corrosion resistance. It contains high amount of Niobium which forms a passive oxide film against corrosion. Heat treatment caused the DMLS Inconel 718 to isotropy nature with more uniform austenitic microstructure and electrochemical corrosion was less than commercial alloy. They concluded that heat treatment improved corrosion resistance against aggressive corrosion environment [104].

From past reported studies it is clear that Ni alloys plays a vital role in aerospace and aviation sector, where there is a need to have good thermal resistivity, corrosion resistance, better mechanical, fatigue and wear properties. Majority of researchers reported the effect of input parameters on mechanical as well as on surface quality of DMLS products. Some of the findings of earlier researchers revealed that post processing improved surface quality, fatigue and creep life.

The effect of build orientation was also studied by few researchers and they found that specimens build in transverse direction (vertical specimens) showed better properties. Limited work published on corrosion resistance of DMLS Nickel alloys. They have high resistance to pitting and Selective Crack Corrosion (SCC) but they have less resistance to intergranular corrosion. Heat treatment at suitable temperatures can increase Ni super alloys corrosion resistance.

There is need to study the impact of different orientations on fatigue as well as mechanical properties. More focus needed to be done on Powder characterization and its effect on properties like part density and surface defects. More literature was present on Inconel 625 and Inconel 718 and maraging steel. Very few works reported on Hastelloy X. Being Ni alloys are relatively costlier and significant engineering materials; DMLS is best AM technique which considerably saves time and material despite of its ability to develop complex parts.

## 2.5 Characteristics of Co-Cr based alloys

In order to produce bio medical parts form Co-based alloys, AM techniques were used in the recent past. Co alloys are high tensile strength and biocompatible material mostly used for medical and turbine engine applications. Cast cobaltbase alloys were originally proposed for surgical implants over 60 years ago. Metallurgical uses of cobalt exploit its properties such as high temperature strength, biocompatibility, high wear and corrosion resistance, magnetic properties, low expansion coefficient etc. It is widely used in gas turbine nozzles, jet engine blades and vanes and hard facing wear resistant applications [105].

Compared to casting AM is more suitable for fabrication of dental prosthesis. In casting material expands and contracts during formation of wax patterns and there is a problem of defects like blowholes which will affect the strength of product. But in this laser sintering process dimensional accuracy is more and dense parts without blow holes can be easily obtained in relatively less time. Additive Manufacturing (AM) can be more productive if the resources used efficiently [106], providing high density and homogeneity in work piece [107], [108].

Co-Cr alloy was used in manufacturing of artificial implants such as hips, knees and bone plates. There are no allergic problems by using Co-Cr alloys, since they are nickel free alloys [109]. These can be used for high load bearing applications due to their high strength and toughness. DMLS could be better choice to make surgical implants from Co-Cr-Mo alloys due to manifestation of increased hardness and uniform microstructure [110]. Cobalt-based alloys finds wide application in other areas like nuclear power plants, rocket fuel nozzles and turbine engine vanes where there is high temperature, oxidation, and hot corrosion [111]. In the field of dental restorations, DMLS is more productive, economic and time saver because it offers good repeatability and faster delivery in the production of metal-ceramic Fixed Partial Dentures (FPDs) [112].

Koutsoukis et al. [113] concluded that DMLS is more time and cost effective process to manufacture dental restorations where it is possible to achieve more or similar properties that we generally obtain by casting or milling. The SEM images of Laser sintered, milling and casted Co-Cr samples were shown in Figure 19.

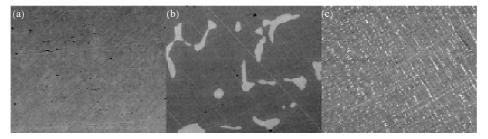


Figure 19. SEM images from the polished cross-section of Co-Cr dental alloys fabricated by a) SLM b) Milling and c) Casting [113]

Puskar et al. [114] used artificial saliva to do comparative corrosion study of DMLS and Cast (CM) Co-Cr-Mo Dental Alloy. They concluded that highest elution observed in high acidic environment and ion release is more in Co. Less elution observed for DMLS alloy in all acidic environments than cast metal. The density variations are shown in Table 1.

Table 1. Density of DMLS and cast (CM) samples [114]

| Sample | Density $\rho(g/cm^3)$ |                      |                  |                    |                    |
|--------|------------------------|----------------------|------------------|--------------------|--------------------|
|        | $ ho_{	ext{average}}$  | $ ho_{	ext{median}}$ | $ ho_{ m stdev}$ | $ ho_{	ext{min.}}$ | $ ho_{	ext{max.}}$ |
| CM     | 8.22                   | 8.22                 | 0.02             | 8.02               | 8.24               |
| DMLS   | 8.60                   | 8.59                 | 0.03             | 8.52               | 8.66               |

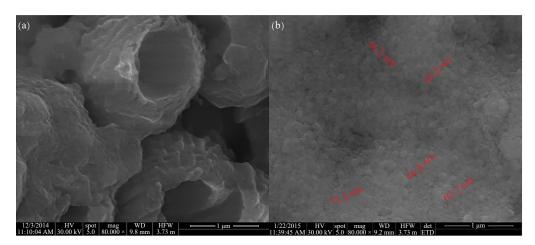


Figure 20. FE-SEM images of sintered sample treated and coated with 2 layers with HA, (a) Before and (b) After immersion in SBF [115]

Diana-Irinel et al. [115] studied the effect of Hydroxyapatite (HA) Ca<sub>5</sub>HO<sub>13</sub>P<sub>3</sub> coating on DMLS Co-Cr samples, they found that the hydroxyl apatite formed after immersion in Simulated Biological Fluid (SBF) is uniform (Shown in Figure 20) and the implants have a better adherence to the bone. The faster healing of the patient was observed. Diana-Irinel [116] used Co-Cr alloy for dental restorations and stated that DMLS was a best process to make dental restorations because part being produced was having limited mechanical stress due to good sinter and mechanical properties of Co-Cr powder. The products made by laser sintering were shown in Figure 21.



Figure 21. Examples of DMLS Dental Bridge and Dental Crown of Co-Cr metal [116]

DMLS Co-Cr-Mo alloy can be used in dental applications because of its excellent mechanical properties like high ultimate tensile strength, the elongation at break and the hardness [117]. The durability of DMLS made dental clasps was superior to that of cast clasps. Additive manufacturing was best technology than dental casting [118]. Josef et al. [119] claimed that DMLS made Co-Cr-Mo dental clasps contain relatively less porosity compared to casted specimens. They can sustain for long time due to higher consistency of retentive forces. The quality of clasps mainly

depends on input laser power, speed and layer thickness which will decide porosity levels and micro structure in the laser sintered part [120] did not affect the mechanical properties of the layered manufactured alloy was not influenced by powder characteristics and the layer thickness [121]. Since DMLS involves utilization of high laser power more heat is generated during manufacturing and rapid cooling also takes place, due to this some thermal stresses will remain in the products, which will lead to thermal strain which is not desirable. So, better strength can be obtained with some post heat treatments [122].

Sing et al. [123] fabricated laser sintered Co-Cr-Mo samples and were solution heat treated. After heat treatment the both Ultimate Tensile Strength (UTS) and Yield Strength (YS) decreased due to carbides formation, but the as built specimens showed twice the values in UTS and YS of casted Co-Cr-MO alloys. Solution heat treatment process showed a great effect on mechanical properties of DMLS Co-28Cr-6Mo alloy, since solution heat treatment increased ductility and reduces yield strength [124]. Solution heat treatment lead to the microstructural transformation which improved its mechanical properties significantly [125].

Co-Cr alloys are widely used in the dental restorations due to their high biocompatibility, high strength and good corrosion resistance. The components manufactured by SLM process contain anisotropic nature non-uniform physical and metallurgical properties. The corrosion behaviour needs to be concentrated more carefully because the release of corrosive products during service can cause adverse health problems. The bio-fluids became aggressive due to presence of oxygen, chloride ions and biological macromolecules during inflammatory conditions [126]. The wear of metal components leads to the dissolution of passive film, so that the body fluids can cause corrosion to Co Cr alloys [127]. Takaichi et al. [128] the selection process parameters will produce different types of dissolved metal ions which will affect SLM Co29Cr6Mo alloy corrosion resistance. According to Liverani et al. [129] concluded that SLM process parameter which resulted in higher mechanical properties determined worse corrosion behaviour. They also proposed low laser power and high scan speed for surface fabrication while high power, low scan speed suggested for bulk material fabrication. The passive film composition on surface of Co-Cr alloy mainly depends on the chemical composition of solution in contact with its surface [130]. So, this can be expected that the alloy will exhibit different corrosion behaviour for different solutions. Electrochemical Impedance Spectroscopy (EIS) indicated that the passive film formed on Co-Cr alloy in 0.9% NaCl solution showed higher corrosion resistance than that was formed in Phosphate Buffer Solution (PBF) [131]. Xin et al. [132] from their studies confirmed that SLM built samples bear the surface microstructural and anti-corrosion properties that meets with the demands of dental clinics.

The Co-Cr metal is best suitable for biomedical applications mainly in dentistry which resulted in porous surface with desired strength. The porous surface is desirable for better adherence with body tissues. The sintered micro structure resulted in better mechanical properties than conventional methods. So DMLS is the best method for fabrication of artificial prosthesis using Co-Cr metals. The corrosion studies indicated that the corrosion resistance of Cr-Co alloy mainly depends on the elements in solution that is in contact with its surface. The process parameters should be controlled properly so that better corrosion resistance can be obtained for SLM products.

The works reported so far on DMLS Co-Cr-Mo mainly focused on the compatibility to use in dentistry. It's a better material for the manufacturing of prosthesis due to its high strength and hardness. Since it is nickel free alloy, it is safe to use in prosthesis preparation. in human body. It is known for its good thermal and corrosion resistance which makes it ideal material for the fabrication of aircraft fuel nozzles and vanes. The load carrying capacity and various methods to improve it should be studied further.

#### 3. Conclusions

The following conclusions are drawn based on works reported by various researchers on DMLS process.

The DMLS made parts were showing better mechanical properties than wrought, cast or forged parts due to fine microstructure observed in DMLS made parts is distinct from the microstructures that observed in conventional manufacturing processes.

Regarding Ti-6Al-4V, from the review it is clear that, it is a light alloy with excellent mechanical properties, low specific weight with good biocompatibility. So it's a suitable material for aerospace and medical fields. Post processing like HIP is required to improve its fatigue strength.

The corrosion resistance of DMLS Ti-6Al-4V is superior/equal to cast or wrought counter parts. The corrosion in Ti alloy is anisotropic nature due to its duplex nature.

For good strength and thermal characteristics AlSi10Mg is the best suitable material in DMLS process. The studies on DMLS AlSi10Mg reported that there is a need to improve surface quality, in order to enhance the fatigue life. The pre heat treatment of build platform showed a considerable improvement of fatigue life and shot peening diminishes surface roughness.

The corrosion behaviour of AlSi10Mg mainly depends on the microstructure formed after corrosion. The T6 heat treatment homogenized the microstructure and there is no selective corrosion attack. The surface quality plays a vital role in its localized corrosion attack.

DMLS Stainless steel exhibits good mechanical properties with better fatigue strength. The laser power and scan speed clearly have impact on their mechanical properties. Post heat treatments showed improvement in their mechanical properties.

The solution heat treatment followed by annealing favors the corrosion resistance against stress corrosion cracking of stainless steel 17-4 PH. Proper heat treatment. The duplex steels are highly susceptible to stress corrosion cracking.

Because of their excellent thermal and corrosion resistivity properties DMLS Ni alloys are playing vital role in aviation and aerospace industries. They retain high strength at elevated temperatures due to precipitation hardening.

DMLS Ni super alloys have high pitting and corrosion cracking resistance. The heat treatment at suitable temperature can improve their corrosion resistance.

Due to superior mechanical properties and bio compatibility of DMLS Co-Cr alloys they mainly used in dentistry to make dental restorations. DMLS is appropriate method for fabrication of implants and dental restorations because there is more design freedom and one can obtain patient specific implants.

The process parameters resulted in higher mechanical properties determines worse corrosion resistance and vice versa.

# 4. Future scope

For DMLS Ti-6Al-4V, there is a need to do explore more about its compressive strength, creep resistance and to find suitable post processing methods to improve its fatigue strength by reducing crack propagation tendency. In order to use it as a successful material in biomedical filed proper methods should be adopted to decrease its elastic modulus despite of losing its strength. There is a need to explore more about degradation mechanism mainly in the contribution of proteins and bio organisms.

For DMLS AlSi10Mg, the surface quality is not up to the desired level. So, researchers should try to find better ways to reduce as-built surface roughness, which is adverse effect on its fatigue strength. There is a need to explore about the effect of surface finishing process over its corrosion studies.

For DMLS Steels concern remains open for better control of input parameters and post heat treatments to extend its applications. Few works reported on its tribological behaviour. Efforts required in reducing the inherent defects like porosity and surface quality to improve corrosion resistance. So the area remained open for future study.

For DMLS Ni based alloys there is need to reduce anisotropy and residual stresses which mainly occurs due to directional solidification and rapid cooling. So, proper build orientation and process parameters optimization could be stimulated. The collapse or depletion of Niobium oxide layer is still a problem in chloride and bromide solutions, which needs to be studied further.

For DMLS Co-Cr alloy the ductility is less, so it's a challenging area for the researchers to work on. Very limited works reported on its dilution nature and corrosion behaviour. There is a need to optimize process parameters to improve its mechanical and corrosion behaviour. The means to improve its corrosion resistance at the interface of metal oxide layer and phosphate solution possibly studied.

# **Conflict of interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.

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