Hardness, Wear and Corrosion Properties of Co-Cr-W Alloy Deposited with Laser Engineered Net Shaping in Medical Applications

Ganzi Suresh; K L Narayana; M. Kedar Mallik

Abstract: ***Laser Engineered Net Shaping (LENS) is promising metal additive manufacturing process used to build near net shape and functionally graded materials. Co-Cr-W alloy samples are fabricated in order to identify the best suitable process parameters for best performing hardness, wear and corrosion resistance to the LENS deposited samples as per the Taguchi L-9 orthogonal array and analysis is carried through the ANOVA and Grey Relational Grade Analysis (GRGA) method. From the experiments, it is identified that the performance of the samples with reference to the above properties is highly influenced by the process parameters. High laser power (350W), moderate powder feed rate (7.5g/min) and high scan speed (20mm/sec) are the optimized process parameters for best performing samples for all the three properties. Further, it draws from the analysis that the influence of the process parameters for laser power (66%), powder feed rate (22%) and scan speed (6%) on best suitable samples for medical applications.***

Index Terms: additive manufacturing, Laser Engineered Net Shaping (LENS), Co-Cr-W alloy, medical implants.

I. INTRODUCTION

Hardness, wear and corrosion properties are very crucial for medical implant application. In general, medical implant devices should possess high mechanical strength, wear resistance and high resistance to corrosion for smooth functioning of the implantable devices without any malfunctioning. Mechanical strength helps to withstand the body weight and gives minimal support to the affected muscle structure. Wear resistance helps to give smooth movement to the implants at joints. Corrosion resistance supports the implants from body fluids and should not release any toxicants during implantation in a human body for a certain period. The fabrication of medical implants is a complex process as medical implants have complex geometry and its structure varies from patient to patient. Hence it is difficult to fabricate medical implants in conventional manufacturing techniques. Additive Manufacturing (AM), is a novel manufacturing technique which helps to fabricate near net shape components, Functionally Graded Materials (FGM's), fully dense and porous structures directly from CAD data, medical images such as CT, MRI and digital X-Rays. It is easy to design and analyse the medical models from the medical images of the individual patients with in less time[1, 2,3,4]. Laser Engineered Net Shaping (LENS), is a metal additive manufacturing process, which uses Nd: YAG laser to melt the powder material and forms the melt pool for the deposition of the models. Amit Bandyopadhyay et al. [5] have demonstrated LENS process for fabrication of medical implants with Co-Cr-Mo alloy. Their study reveals that it is possible to fabricate both dense and porous structures for medical application by controlling the LENS process parameters. Janaki Ram et al. [6] have used LENS to fabricate Co-Cr-Mo alloy and compared the test results with conventional manufacturing process and found that LENS processes samples are superior in mechanical strength and wear. Achieved fine microstructure extremely fine microstructures, with a comparable carbide volume fraction and hardness to Co-Cr-Mo wrought materials. LENS deposited Co-Cr-Mo exhibits a carbide morphology with very thin, long interconnected carbide particles. Mantralaet al. [7] LENS deposited Co-Cr-Mo alloy by varying the process parameters and tested the samples for both with and without heat treatment. Suresh et al. [8,9,10, 11] have studied the biocompatibility of LENS deposited Co-Cr-W alloy. It has been identified that the alloy samples result in a positive response to cellular activity during the experimental period of 24-72 hours. MTT assay demonstrated that cell availability is superior in Osteoblast cells compared to the Fibroblast cells. Osteoblast cells showshigher viable to the cell treatment on the samples. Sub chronic toxicity study reveals that the alloy samples didn't produce any toxic signs or evident symptoms. From this study it is concluded that the Co-Cr-W alloy is suitable for medical applications.

In the present work an attempt is made to identify the best suitable process parameters in fabricating best performing Co-Cr-W alloy for hardness, wear and corrosion resistance in medical applications.

II. MATERIALS & METHOD

Commercially available Co-Cr-W alloy (Stellite – 6, Kennametal, GmbH Germany) powder with particle size ranging 38 – 150 µm, is utilized to fabricate samples on Laser Engineered Net Shaping (MR-750, Optomec Inc., Albuquerque, NM, USA).

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Ganzi Suresh, Department of Mechanical Engineering, Koneru Lakshmaiah Education Foundation, Guntur, India

K L Narayana, Department of Mechanical Engineering, Koneru Lakshmaiah Education Foundation, Guntur, India

M. Kedar Mallik, Vasireddy Venkatadri Institute of Technology, Namburu, Guntur, India.

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Table 1 shows the chemical composition of Co-Cr-W alloy.

Table 1: The composition of Co-Cr-W alloy in weight %

Elements	Composition
Cobalt (Co)	Base
Chromium (Cr)	28.0-32.0
Tungsten (W)	4.0-6.0
Carbon (C)	2.0-3.0
Silicon (Si)	1.2
Nickel (Ni)	1.0
Iron (Fe)	1.0

By L-9 Orthogonal Array Three sets of samples are fabricated (Table 2) on a Fe-Cr-Mo alloy substrate or base plate to have metallurgical bonding during deposition. Each set of samples is used to test the hardness, wear and corrosion resistance.

Table2: L-9 Orthogonal Array for depositing Co-Cr-W alloy at three different levels

Sample ID	Laser Power 'W'	Feed Rate 'g/min'	Scan speed 'mm/sec'
1	200	5	10
2	200	10	15
3	200	7.5	20
4	275	5	15
5	275	10	20
6	275	7.5	10
7	350	5	20
8	350	10	10
9	350	7.5	15

Instrumented micro hardness tester (IMHT Anton Paar Tritech, Swiss) was employed to study the Vickers hardness with a pyramid diamond indenter at 5N load applied for 10Sec on different layers of deposition along the build direction from the bottom to the top of deposition.

Wear resistance tests are carried on the samples using Pin on disc tribometer (Ducom India Pvt. Ltd.) at three specific loads (10, 20, 30N) and speeds (100, 200, 300rpm). The LENS deposited samples are used as pins and a circular plate of EN31 steel is used as disc., the wear test is carried for a 3km by keeping the track diameter as constant samples run under dry wear and metal to metal contact settings. The surface of the disc is cleaned for every run with acetone for the leftover particle of the samples and reading are noted at three different loads and speeds.

Electro chemical work station *CH Instruments*, Inc., USA (700C PotentioStat) was employed to test the electrochemical corrosion of the samples. Hanks solution[12] with pH 7.3 is simulated body fluid habitat at 37±1°C which is similar to that of human body temperature. Corrosion test is carried with a three-electrode cell in which a working electrode is Co-Cr-W (test sample), the counter-electrode is high-density graphite and saturated calomel electrode (SCE) is the reference electrode. The cyclic potentio-dynamic polarization techniques used to evaluate pitting corrosion of Co-Cr-W deposits.

Analysis of variance (ANOVA) was performed on experimentally obtained hardness, wear and corrosion resistance for best performing samples with three process parameters. The present work focuses on identifying the optimized combined samples which can provide high hardness and low wear rate and low corrosion rate. Grey Relation Grade Analysis (GRGA) is carried out to identify the best sample for higher hardness, lower wear rate corrosion rate[13]. Again, ANOVA was done on the grade obtained from GRGA to identify the influence of process parameters on the results.

III. RESULTS & DISCUSSION

The micro-indentation measurements for the hardness are listed in Table 3. It is observed that overall hardness of LENS deposited samples is ~50 -100 HV higher than that of conventionally processed Co-Cr-W alloys. From the table it is evident that hardness of samples1-3 processed at 200W laser power are higher than that of samples 7-9 processed at 350W. Lower laser power implies a low energy density and high cooling rate which in turn influences the grain structure and phase formation during solidification. Also, at lower laser powder and moderate powder feed rate the powder particles are not completely melted as the availability of powder for deposition is more and as the scan speed is high, overlapping of grains occur which leads to high hardness. The study of hardness at different layers reveals that the hardness is very low at the layers nearer to the substrate due to the influence of the substrate, which also melts along with the powder during deposition of first few layers. Similarly, due to the rapid solidification rate, the hardness on top layers is also identified to be less when compared to the middle layers.

The wear resistance test results are shown in Table 3. From the table it has been observed that the rate of wear resistance of the samples varies from 1.5E-7g/Nm to 5.5E-7g/Nm. Which is incompatible with the as cast samples of Co-Cr-W alloy samples. It is clearly observed from the tests, when the load is increased, the more is wear loss, it is further noted with an increase in either load or speed of the test the wear rate decreases. The highest wear rate has been reported at 10 N load and 300 RPM speed (5.5E-7g/Nm).

The corrosion rate is calculated from the corrosion potential (E_{corr}) and corrosion current (I_{corr}) of Co-Cr-W alloy samples derived from respective Tafel plots are summarized in Table 3.Sample 8 and 9 shows high corrosion resistance at high laser power, high powder feed rate and low scan speed. It is due to the Cr-carbides are accumulated along with the grain boundaries of cobalt. Due to difference in powder feed rate and scan speeds for both samples 7 and 9 samples show different corrosion rate even there is similar laser power. The process parameters like powder feed rate and scan speed influence the formation of different grain size which leads to different corrosion rates. Carbides formed at boundaries are strong enough to withhold the current to pass through the grain by grain in sample 8 and 9, so they show high resistance to corrosion.

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Table 3: Test results of hardness, wear and corrosion rate

Sample Id	Hardness (Vickers)	Wear Rate (g/Nm)	Corrosion Rate (mpy)	Grade
1	528±49	4.0E-07	2.703×10^{-1}	0.5561
2	545±17	5.0E-07	3.257×10^{-1}	0.5637
3	562±20	5.5E-07	1.570×10^{-1}	0.7091
4	491±42	4.5E-07	3.594×10^{-1}	0.4542
5	543±46	3.5E-07	4.924×10^{-1}	0.5615
6	528±48	2.5E-07	9.108×10^{-1}	0.5215
7	529±18	2.0E-07	3.227×10^{-1}	0.6584
8	511±58	3.0E-07	0.449×10^{-1}	0.6790
9	473±55	1.5E-07	0.577×10^{-1}	0.7681

ANOVA is carried out to identify the influence of process parameters on the performance characteristics of hardness, wear and corrosion rate. Main effect plots for hardness, wear and corrosion rate are shown in Fig. 1. It is observed from the main effect plots that to achieve the best hardness, the following process parameters are identified as laser power with 200W, feed rate 10g/min and scan speed 20mm/sec. Similarly, for a best performing wear rate low laser power with 200W, high feed rate 10g/min, and high scan speed 20mm/seas are most influencing. Finally, for the corrosion rate medium laser power 275W, medium powder feed rate 7.5g/min and low scan speed 10mm/sec.

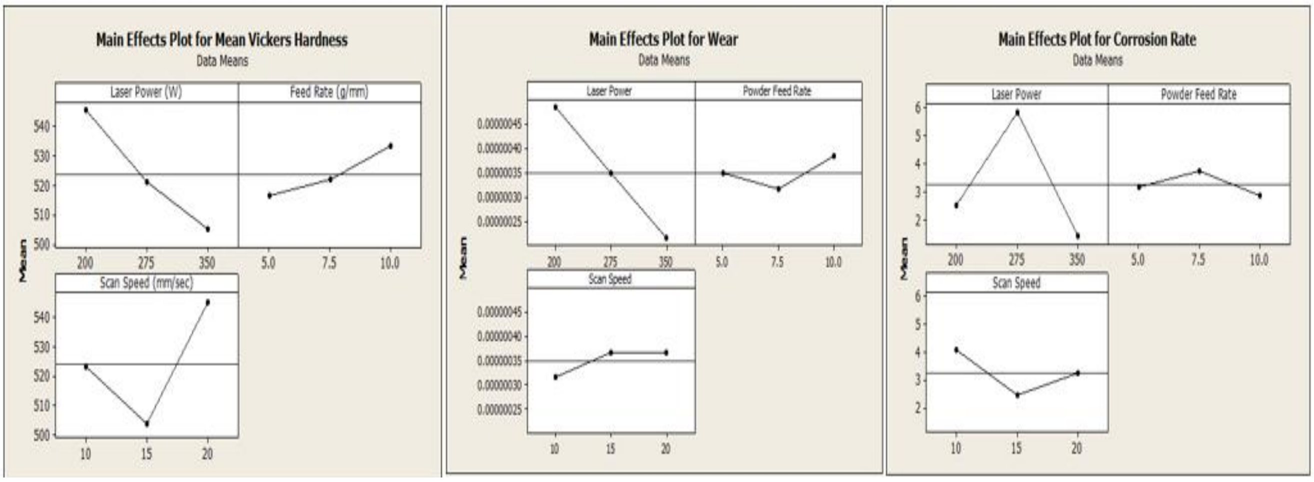

Figure 1: Main effect plots forhardness, wear and corrosion rate

Grey relation grade analysis was used to optimize multi-performance characteristic value into a single Grey Relational Grade value. It is to be known that the perception of grey relation analysis defines that the grey relation grade value is higher and then the process parameters are closer to its optimized value. After identifying the grey relation grade values, a response table was developed with grey relation grade as in Table.4. As there are three process parameters three factorial levels are assumed. Each level is considered with mean grade values at respective process parameters. For example, for level 1 grade values of laser power at 200W (0.5561, 0.5637, 0.7091) is mean of corresponding grade values (0.6096). Similarly, of the entire table is developed.

Table 4: Response table of Grey Relation for hardness, wear and corrosion rate

Symbol	Process Parameters	Grey relation grade Level-1	Level-2	Level-3	Main Effect (Max-Min)	Rank
A	Laser Power	0.6096	0.5124	0.7018*	0.1894	1
B	Feed Rate	0.5562	0.6014	0.6662*	0.0648	2
C	Scan Speed	0.5855	0.5953	0.6430*	0.0575	3

At the level-1 setting parameter, the laser power shows a higher value with 0.6096 next scan speed with 0.5855 and least one is feed rate with 0.5562. At level-2, feed rate is higher value with 0.6014, scan speed is second highest value with 0.5953 and laser power is the least value with 0.5124. Finally, level-3 show the laser power higher value with 0.7018 next is the powder feed rate with 0.0.6662 compared to the scan speed with 0.6430 is less value, respectively. The main effect is calculated by subtracting the maximum and the minimum values of mean grey relation grade from each level of process parameters. The main effect plot is drawn for responses from the grey relation shown in Fig. 2. It shows that high laser power (350W), medium powder feed rate (7.5g/min) and high scan speed (15mm/sec) are the most performing process parameters for best outputs.

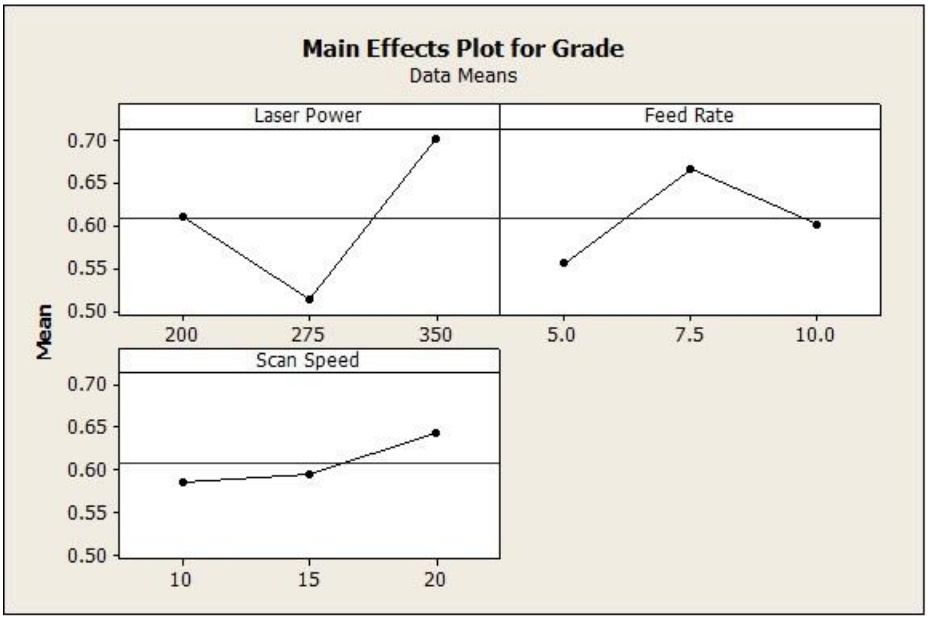

Figure2: Main effect plot of Grade analysis forhardness, wear and corrosion rate

Ranking is made with maximum grade value to minimum grade value of the main effect. Ranking the process parameters with higher to lower values from the main effect. Laser power (0.1894) has the most effect on the grey relation grade, second is the powder feed rate (0. 0648) and finally scan speed (0. 0575) shows the lowest effect. This will be additionally affirmed through the measurable investigation by ANOVA, the optimized process parameter for three levels can be identified corresponding to the highest value of the grey relation grade. Response chart for Grey relation grade is shown in Fig. 3. Therefore, the best process parameter has been identified from the above study is the A3B3C3, in which the laser power is at 350W, the feed rate is 7.5g/min and scan speed is about 20mm/sec. The optimized process parameters for three different levels identified and plotted according to their highest value of the grey relation grade as shown in Fig. 3.

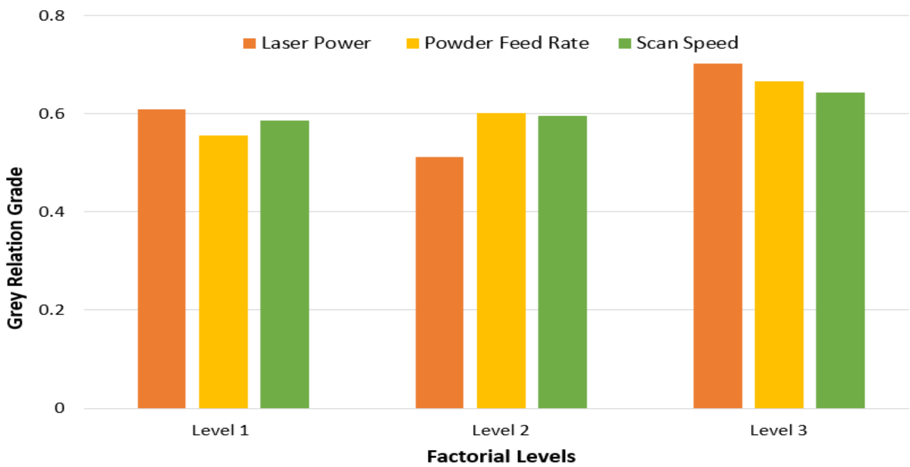

Figure3: Response chart for Grey relation grade of hardness, wear and corrosion rate

Analysis of variance (ANOVA) is further conducted for the responses of grey relation to identify the most performing process parameters. Commonly ANOVA is used to assess the contribution of each process parameters from the experimentally determined values. At first, the ANOVA is performed through the calculation of the sequential sum of squared, adjacent sum of squares and adjacent mean of squares from the total mean of the grey relational grade. Subsequently the effect of each experimental parameter can be separated according to the contributions and error of each process parameter. Any parameter that presents the highest mean square value is treated as the most important process parameter that affects the multiple performance characteristics. The result of ANOVA is shown in the Table. 5. It is observed that the laser power is considered as the most significant factor as it represents 66.17%, the powder feed rate represents 22.53% and scan speed is 6.89% of the consolidated commitment towards the various test yields.

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The error that may due to the combined effect of experimentally driven from this ANOVA test was 4.32%, which is statistically acceptable.

Table 5: ANOVA results based on the Grey Relational Grade for hardness, wear and corrosion rate

Process parameters	**DOF**	**Seq SS**	**Adj SS**	**Adj MS**	**F ratio**	**P ratio**	**Percentage of Contribution (ρ)**
Laser power(A)	2	0.0538	0.0538	0.0269	15.23	0.062	66.17
Feed rate(B)	2	0.0183	0.0183	0.0091	5.19	0.162	22.53
Scan speed(C)	2	0.0056	0.0056	0.0028	1.6	0.384	6.89
Error	2	0.0035	0.0035	0.0017	-	-	4.32
Total	8	0.0812	0.0812	0.0405	-	-	100

IV. CONCLUSION

The present work showcases the fabrication of Laser engineered net shaping deposited Co-Cr-W alloy as per the L-9 orthogonal array. The conclusions drawn from the experimentation are as follows.

1. High hardness is achieved for the samples at low laser power, moderate powder feed rate and high scan speed. It is due to the partial melting of powder particles, availability of excess powder and overlapping of grains, which leads to higher microhardness.
2. The wear resistance was found to be compatible with as-cast Co-Cr-W (Maximum wear rate: 5.5E-07g/Nm).
3. It is observed that samples-7 shows high pitting corrosion and samples 8 and 9 are high resistance to corrosion, it is due to the influence of process parameters at different conditions, which is below standard corrosion rate of ASTM F 2129.
4. From ANOVA, it is observed that high laser power (350W), moderate powder feed rate (7.5g/min) and high scan speed (20mm/sec) are desired to get the best of three properties (hardness, wear and corrosion rate) studied.
5. Grey relation grade analysis (GRGA) shows the order of high influencing factors and percentage of contribution of each process parameter in depositing the optimized samples as most influencing is laser power (66%) next is the powder feed rate (22%) and finally scan speed (6%) is less influential.

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