ENHANCEMENT OF WEAR RESITANC OF MAGNESIUM ALLOY BY USING SURFACE MODIFICATION

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Abstract: Materials play an important role in the development of product for many applications. Biomaterials are the class of materials abundantly used as dental implants, orthopedic implants, tissue replacements, supports, replacement of joints in human body parts like HIP, Knee etc in biomedical field. Biomaterials are biocompatible which are having an appropriate response with the host for a specific application. As these members are prone to physiological conditions in the human body, they tend to fail because aseptic loosening caused by the per prostheticosteolysis. The studies shown that the cause for the osteolysis is wearing debris of biomaterials.In order to improve the tribiological characteristics like corrosion and wear, to increase the life span of these biomaterials, their surface is to be modified. In this work an attempt has been made to improve the tribological characteristics by modifying the surface through thin film coatings. Tests are performed to know the behavior of modified biomaterials and also a comparison is made between the coated and uncoated materials . It is observed that there is a significance improvement in corrosion and wear of coated Mg alloy compared to uncoated Mg alloy.

***Index Terms* – Bio materials, orthopedic, osteolysis.**

I. INTRODUCTION

The commercially available Mg-based biodegradable implants have been new in the market dating back to 2010s. Magnezix (brand name of Mg-based implant in the market) is the first approved and CE-certified biodegradable screw that has been manufactured using PM route. It has been approved for bone fixation and fragments . It has more appropriate mechanical properties than commercially available Ti. For instance, owing to its close elastic modulus to natural bone, it hinders stress shielding that could even cause implant loosening. Moreover, it is free of Aluminum (Al), therefore, it is less likely to show any allergenic or toxic side effect. Magnezix has a yield strength (YS) greater than 260 MPa, a ultimate tensile strength(UTS) greater than 290 MPa and an elastic modulus about 45 GPa. It has an ability to elongate as high as 8%. After material and product design study started in 2009 for Magnezix preclinical studies were conducted between the years 2010 and 2012 . The Magnezixwas approved by CE certification for 30 days in May 2013. It was put first in EU market and then the rest of the world. It has been reported that more than 4000 Magnezixscrews were sold around the world since then. The company continued to expand their product range with different screw sizes.

Commercially available Mg-based implants have been compared with other biodegradable and non-Mg implants. They have been tried by in vivo studies as well. They have been implanted in 33 mini-pigs and 20 humans . No toxicityor allergenic reactions were observed. They preserved mechanical integrity themfor six months that could be regarded as long-term for fixation implants. After that, three generations of absorbable metal stents have successfully been implanted into animals and humans. Schmidt et al. compared three biodegradable stents namely: The Absorb GT1 (Abbott Vascular, Temecula, CA), DESolve (Elixir Medical Corporation, Sunnyvale, CA) and the Magmaris (BIOTRONIK AG, Bülach, Switzerland). The Absorb GT1 and DESolve are made of polymers whereas Magmaris is an Mg-based PLLA coated stent. They were successfully approved in clinical trials. According to the tests, Magmaris expanded quickly and it was more stable in terms of mechanical performance. Although all the stents had sufficient radial strength, metallic one had the highest. Windhagen et al. conducted a comparison study between Magnezix and Ti screws in 26 patients to assess their difference regarding patience comfort and biological effect during an implantation period of six months. It was reported that there was no statistically significant difference between two types of screws in terms of human comfort and poor biological reaction. All patients were satisfied with the Magnezix except one patient who had suffered from long-last wound problem . It showed that there was no distinct difference in terms of functionality but second surgical operation for implant removal was abolished for Mg based material.

II LITERATURE REVIEW

P. C. Innocenzi et al (1992) has worked on four metals Ni, Fe, Al and Cu. These metals are coated with ZrO_2, TiO_2, SiO_2, or B_2O_3-SiO_2 films. Good quality coatings are obtained on Ni and Al by compared with Fe and Cu metals. Innocenzi used the aged solutions to get a better improvement. By using weight gain and X-ray diffraction measurements the oxidation resistance of coated Ni and Cu samples was examinated. In the case of Ni metal compared with previously corrode substrate at 800° C with a borosilicate coating a substantial improvement of its oxidation resistance was obtained. By increasing the thickness some improvement may be achieved, but there is a limit over which occurs crack formation and the protective action is reducing.

Massimo Guglielmi et al (1997) has worked on the sol-gel coatings on metals. Massimo Guglielmi says that the coating on metals it may protect from oxidation. The liable elements should be deliberate as a possible to barrier layers by depositing the homogeneous films. In this occasion, thicker and crack free coating have to be produced. Naturally converted films may be a solution for low temperature applications. For coating complex metallic substances the sol-gel coating methods i.e., dip and spin coating are not convenient. Alternative techniques should be experimented or developed, in order to give better chances for application.

D. M. Kennedy et al (1998) has carried out the wear tests with a high degree of simulation of the service situation, and then the results can be used with reasonable conviction in selecting the best wear-resistant coating system. For the hugeness material or coatings every wear test can be difficult by equipment problems, sample preparation, test procedures, variance in abrasive materials and the wrong apprehension of the test information. In order to avoid diffusion thin coatings require greater care in wear tests, which requires shorter test durations and lighter loads.

From the above literature it is observed that the plasma spray coating is showing positive impact on the coating characteristics and its faster manufacturing makes it a choice for coating of materials for biomedical applications. In the next chapter, the surface modification techniques are briefly illustrated.

III Substrate Preparation:

Substrate preparation is a very crucial step in thermal spraying. In this study, ZM21 magnesium alloy each measuring 40mm × 30 mm × 6 mm were prepared as shown in fig 4.1. The specimens were polished by different grades of silicon carbide papers (180 to 1200 grit) followed by cloth wheel polishing with diamond paste on a polishing machine

FIG 3.1ZM21 Mg alloy

Element	**Mn**	**Zn**	**Mg**
Composition(%)	1.08	2.0	96.92

Table 3.1.Composition of ZM 21 Mg alloy

3.1 Samples before coating:

From the square shape of ZM21 Mg metal the metal cutting into required shape.The fig.4.2. shows the ZM21 Mg metal substrates before coating.Samples used in this study were ZM21 Mg alloy prepared in square shape with the dimension of 40 x 30 mm and the thickness is 6mm.To obtain more reliable results, repeatability of process, for each series of experiment at least 2 samples were used. The samples are cleaned with emery papers.

Figure 3.2:Mg-alloy substrates before coating

3.2.Synthesis procedure:

The synthesized product was obtained from titanium (IV)isopropoxide, ≥97% (Sigma Aldrich) dissolved in ethanol(Merck) and deionized water was added to the solution in molar ratio of Ti:H2O = 1:4. The mixed solution was vigorously stirred for 1 h in order to form sols. After aging for a day, the sols were transformed into gel form. The obtained gels were dried at 120°C for 24 h to remove the water and organic materials. After that, the dried gel was sintered at 450ºC for 2 h in homemade high temperature programmable furnace. Finally the pure TiO2 nanoparticles were obtained.

3.3. Preparation of Sol-Gel Solution:

Titanium tetra isopropoxide**($Ti\{OCH(CH_3)_2\}_4$),** Ethanol (C_2H_5OH) and Deionized Water (H_2O) are having different molar ratios, molecular weight and density. From these values weight is calculated. From the weight and density volume is evaluated. Based on volume of each solution the solutions are added and mix up to prepare the sol-gel.

3.4 Procedure for plasma spray coating:

- Material goes for cleaning
- Masking
- Blasting
- Plasma room

The Plasma Spray Process is basically the spraying of molten or heat softened material onto a surface to provide a coating. Material in the form of powder is injected into a very high temperature plasma flame, where it is rapidly heated and accelerated to a high velocity. The hot material impacts on the substrate surface and rapidly cools forming a coating. This plasma spray process carried

out correctly is called a "cold process" (relative to the substrate material being coated) as the substrate temperature can be kept low during processing avoiding damage, metallurgical changes and distortion to the substrate material.
The Plasma Spray gun comprises a copper anode and tungsten cathode, both of which are water cooled. Plasma gas (argon, nitrogen, hydrogen, helium) flows around the cathode and through the anode which is shaped as a constricting nozzle. The plasma is initiated by a high voltage discharge which causes localized ionisation and a conductive path for a DC arc to form between cathode and anode. The resistance heating from the arc causes the gas to reach extreme temperatures, dissociate and ionise to form a plasma. The plasma exits the anode nozzle as a free or neutral plasma flame (plasma which does not carry electric current) which is quite different to the Plasma Transferred Arc coating process where the arc extends to the surface to be coated. When the plasma is stabilised ready for spraying the electric arc extends down the nozzle, instead of shorting out to the nearest edge of the anode nozzle.

Plasma spraying has the advantage that it can spray very high melting point materials such as refractory metals like tungsten and ceramics. Plasma sprayed coatings are generally much denser, stronger and cleaner than the other thermal spray processes with the exception of HVOF, HVAF and cold spray processes. Disadvantages of the plasma spray process are relative high cost and complexity of process.

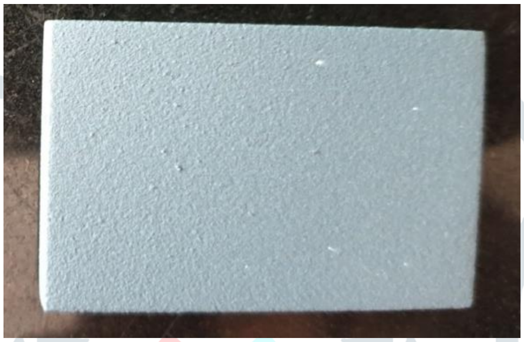


Figure 3.3: After coating ZM21 Mg alloy

IV WEAR TESTING

The setup of the method comprises of a pin with spherical surface as the tip and a circular rotating disk which is placed at a perpendicular with respect to the spherical pin surface. The surface of the pin is 11 X 11 mm^2 and the length is 5 mm. The disk is made of hardened steel on which the pin is held with a jaw in the apparatus and rotation is provided to disk which causes wear of the pin on a fixed path on diskThe pin is pressed against the surface of the disk with load being applied with the arm attachment provided to the apparatus. Machine is attached with a data acquisition system and WINDUCOM 2010 software which gives result values as noted in table.4.1

Working Parameters:
Wear track radius: 47.74, 39.78 mm
Load applied: 2, 3 and 4 kg
Time Duration: 5 min
Rotation of disk: 500, 600 rpm
Pin Size: 11x11 mm^2

SI.No	ZM21 Metal	SpeedN (rpm)	Load(kg)	Time(min)	Track radiusR (mm)
1	Without Coating (Sample 1)	500	2	5	47.74
2	With Coating(Sample 2)	500	2	5	47.74
3	With Coating (Sample 3)	600	3	5	39.78
4	With Coating (Sample 4)	600	4	5	39.78

Table. 4.1 Tabular column for wear test Parameters:

Here Track radius is calculated by using the formula $V = \pi DN / 60$ or $\pi(2R)N / 60$ m/s

Sample 1 and 2:

Here Sliding Velocity V = 2.5 m/s , N = 500 rpm
$V = \pi(2R)N / 60$ m/s
$2.5 = \pi \times 2 \times R \times 500 / 60$ m/s
Therefore $R = 2.5 \times 60 / \pi \times 2 \times 500$ m
= 0.04774 m or 47.74 mm

Sample 3and 4:
Here Sliding Velocity V = 2.5 m/s , N = 600 rpm
$V = \pi(2R)N / 60$ m/s
$2.5 = \pi \times 2 \times R \times 600 / 60$ m/s
Therefore $R = 2.5 \times 60 / \pi \times 2 \times 600$
$= 0.03978$ m or 39.78 mm.

V.RESULTS AND DISCUSSION

The titaniumdioxideNano particles are coated on the ZM21 Mg alloy substrates with 100µm thickness by Plasma Spray coating method.

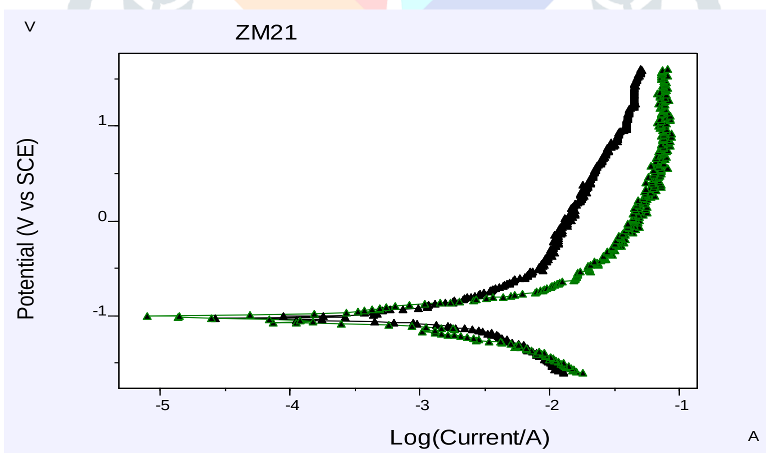
5.1. Corrosion resistance test:

For corrosion resistance testing, both the coated and uncoated samples are considered. Before and after the testing the samples are shown in fig 6.1 and fig 6.2. The graph between potential (V vs SCE) and log (current /A) as shown in graph 6.1.

Figure 5.1. Uncoated material after testing   Figure 5.2.Coated material after testing

The experiment is conducted between samples containing titaniumdioxide nanoparticles and samples without titaniumdioxide Nano particles.

The final result is by comparing the results from uncoated sample and coated sample, the coated sample containing titaniumdioxide nanoparticles have good performance of corrosion resistance than uncoated sample.



5.1. Graph between Potential vs Current

Uncoated material: GreenCoated material: Black

5.2 Corrosion behavior:

The corrosion behavior of Plasma Spray coatings evaluated by potentiodynamic polarization technique after exposure of 300ml hanks solution is presented. The corrosion potential (E/mV) on Y-axis, corrosion current density (I/mA) on X-axis. The corrosion potential of ZM21 Mg alloy with a Titanium dioxide Nano particlespowder based plasma spray coating was found to be slightly active than the uncoated magnesium substrate.

The possible explanation for electrochemical corrosion determinations several and even many times lower than the corrosion rates directly determined by gravimetric measurements, hydrogen evolution, or other methods is the anomalous chemical dissolution process, occurring simultaneously with the normal electrochemical corrosion attack.

Since chemical reaction cannot be followed by electrochemical means, the electrochemical methods might give much smaller corrosion rates than those determined by weight loss measurements, volume of hydrogen gas, or amount of corrosion products in solution as a function of the immersion time.

Finally, the use of the Stern-Geary equation for the electrochemical estimation of the Polarization Resistance (Rp) is given by

$$Rp = \frac{B}{i_{corr}}$$

Where Rp is the charge transfer resistance, presents two main challenges: the precise knowledge of the B constant

$$B = \frac{\beta a + \beta c}{2.3\,(\beta a + \beta c)}$$

. The constants $\beta a$and βc are evaluated based onTafel plots.

These Tafel plot values are obtained by plotting slopes. By using Origin software the data is generated based on the values for uncoated Mg alloy and coated Mg alloy. Ec lab software is used to calculate the corrosion rate from Tafel plots.

5.3 Tafelparameter for uncoated ZM21 alloy:

Table 5.1 Tafel parameters for ZM21 Mg alloy:

Specimen	E_{corr} (mV)	I_{corr} (μAcm^2)	βa (mV/dec)	βc(mV/dec)	Corr. Rate (mmpy)
ZM21 Mg alloy	-1041.092	130.929	139.3	43.9	0.453
ZM21 Mg alloy	-1030.73	306.956	235	131.8	0.311

5.4 Tafel parameter for Coated ZM21 alloy:

Table 5.2.Tafel parameters for coated ZM21 Mg alloy:

Specimen	E_{corr} (mV)	I_{corr} (μAcm^2)	βa (mV/dec)	βc (mV/dec)	Corr. Rate (mmpy)
Titanium dioxide Nanoparticlescoated Mg alloy	-1023.424	61.19	111.8	148.6	0.127
	-1015.457	72.015	111.0	96.5	0.119

VI CONCLUSIONS

In the present our project work ZM21 Mg alloy is coated with titanium dioxide Nano particles by using Plasma spray method. The corrosion test on coated samples and uncoated samples is performed by using electrochemical test.ZM21 Mg alloy coated with titanium dioxideNano particles exhibit good corrosion resistance comparing samples without titanium dioxideNanoparticles. The percentage of improvement in the corrosion resistance is about 72%.

Table 6.1 Comparison is made between the coated and uncoated Mg alloys

6.2.

Specimen	E_{corr} (mV)	I_{corr}(μAcm^2)	βa (mV/dec)	βc (mV/dec)	Corr. Rate(mmpy)
ZM21 Mg alloy	-1041.092	130.929	139.3	43.9	0.453
	-1030.73	306.956	235	131.8	0.311
Titanium dioxide Nano particles coated Mg alloy	-1023.424	61.19	111.8	148.6	0.127
	-1015.457	72.015	111.0	96.5	0.119

FUTURE SCOPE

1.The work can be extended to improve the Tribological properties.

2.The porosity and grain structural modifications may also be carried effective functioning under the conditions.

3.Medical and automotive applications.

4.To observe the microstructure difference between coated sample and uncoated samples.

REFERENCES

1. P. C. Innocenzi, M. Guglielmi, M. Gobbin, P. Colombo, "Coating of Metals by the Sol-Gel Dip-coating Method", Journal of the European ceramic society 10 (1992) 431-436.
2. Massimo Guglielmi, "Sol-Gel Coatings on Metals", Journal of Sol-Gel Science and Technology 8, 443-449, (1997).
3. D. M. Kennedy, M.S.J. Hashmi, "Methods of wear testing for advanced surface coatings and bulk materials", Journal of Materials Processing Technology 77 (1998) 246-253.
4. K. Umanath, S. T. Selvamani, K. Palanikumar, T, Raphael, K. Prashanth "Effect of Sliding Distance on Dry Sliding Wear Behaviour of Al6061/SiC/Al_2O_3 Hybrid Composite", Proc. of Int. Conf. on Advances in Mechanical Engineering, AETAME, (2003).

5. Duhua Wang, Gordon, P. Bierwagen, “Sol-gel coatings on metals for corrosion protection”, Progress in Organic Coatings 64 (2009) 327-338.
6. Rong-Gang Hu, Su Zhang, Jun-Fu Bu, Chang-Jian Lin, Guang-Ling Song, “Recent progress in corrosion protection of magnesium alloys by organic coatings”, Progress inOrganic Coatings 73 (2012) 129-141.
7. Deepak Kumar, Jayant Jain, TulsiBisht, AmizZindal, “Effect of Precipitates on
8. Mechanical and Tribological Performance of AZ91 Magnesium Alloy-Steel Couple”, Journal of Tribology, Vol. 137, April (2015).
9. NajmeLari, ShahrokhAhangarani, AlinShanaghi “Effect of Different TiO_2-SiO_2 Multilayer Coatings Applied by Sol-Gel Method on Antireflective Property”, Journal of
Materials Engineering and Perfoemance, Vol. 24, No. 7 (2015).

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