METHODS TO IMPROVE WEAR RESISTANCE AND REACTIVITY OF MAGNESIUM AND ITS ALLOYS BY SURFACE ENGINEERING TECHNIQUES

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ABSTRACT:
Magnesium and its alloys, has one quarter of density of steel & two-third density that of aluminium (from 1.75 to 1.85 gm/cm$^3$). It also has a high strength to weight ratio along with an attractive bulk of mechanical properties. Hence it fulfils the role of an ‘ULTRA LIGHT WEIGHT ALLOY’. This results in usage of magnesium alloys in applications field like microelectronics, aerospace, automobile applications etc. But still there is a presence of relatively poor resistance to wear and also high reactivity, which hampers its wider applications. These factors can be avoided by three methods. In First method, Laser treatment of magnesium alloys with Al$_2$O$_3$+Al is done. In this method, laser processing of 10 kW continuous waves of Co2 melts substrate of MEZ & subsequently feeds Al+Al$_2$O$_3$ which increase its hardness. Electro less Nickel plating is the second method. Here deposition of alloying material is investigated by scanning electron microscopy & plating by galvanic coupling of beta phase & alpha eutectic phase. Third method includes of Nanoparticles based on inorganic coating. In this method, nanoparticles of high sintering activity allows to obtain inorganic coating at low temperature along with silicon dioxide nanoparticles deposition resulting in high hardness, crack free layers and corrosion free surface.

Keywords: Nickel plating, eutectic phase, inter dendritic spacing, micro hardness.

1. INTRODUCTION
Magnesium and its alloys, with one quarter of the density of steel and only two-thirds that of aluminium and a strength to weight ratio that far exceeds either of these, hence have a wide scope of applications in the field of automotive and aerospace industries. Magnesium alloys are increasingly used nowadays in applications where a reduction of weight without a loss in stability is required. They mainly feature with exceptional properties like low densities (from 1.75 to 1.85 g/cm³) and high specific strength. And also with high purity, good resistance to atmospheric corrosion. Despite this attractive range of bulk mechanical properties, a relatively poor resistance to wear is a serious impediment against wider application of magnesium alloys. Along with wear, due to their high reactivity these alloys require a good protection against corrosion. Thus there is a serious limitation for the potential use of several magnesium alloys in their respective engineering fields. Thus to counter these degradation in magnesium alloys, several surface engineering techniques were introduced which not only fixed these problems but also improved its further characteristics. Ceramic coatings with help of laser surface engineering, electro less nickel plating, nanoparticles based inorganic coatings, chromating are some of these techniques. These processes mainly reduce wear and corrosion by appropriate tailoring of the surface microstructure and composition without affecting the bulk.

2. APPLICATIONS OF MAGNESIUM ALLOYS
a. Magnesium alloy has wider influence in automobile industries for example such as engine blocks or power train components along with reducing the total weight of automobile like in gear box housings and crank cases.

b. In aerospace field, magnesium alloy is used in welded or bonded airframes; use of metal laminates; structural plastics; fibre reinforced composites and exhibit good strength and stiffness at both room and elevated temperatures.

c. Commercial applications include hand-held tools, luggage, computer housings, and ladders.

d. In bicycles industries too, the metal matrix composite is used in the bicycle industry due to its excellent stiffness and reduced weight compared to aluminium

e. Magnesium alloy is also being used in medical field for cardiovascular and orthopaedic medical device applications along. Magnesium alloy materials have also been used for different types of fixation devices for orthopaedic surgery, such as screws, plates, and fasteners.
Figure 1 Some automotive components made of Mg alloy and obtained weight reduction

3. SURFACE ENGINEERING TECHNIQUES

3.1. LASER SURFACE ENGINEERING OF A MAGNESIUM ALLOY WITH Al+Al2O3

a) Experimental details:
MEZ, a magnesium alloy is chosen because of their potential scope of application as automotive components in the engine and gear section. Laser surface modification was carried out with a 10-kW continuous wave (CW) CO2 laser, having a beam diameter of 4 mm by melting of MEZ substrate and simultaneous feeding of a mixture of Al (of particle size q40 to 60 mm) and Al2O3, in the ratio of 3:1 using Argon as shrouding gas. The specimens were mounted on a water chilled copper block placed on a CNC controlled X–Y stage which was moved at a speed of 50–1000mm/min.

A relative speed between the laser beam and the specimen was maintained to control the substrate–laser beam interaction time and larger area coverage. To achieve microstructural and compositional homogeneity of the laser treated surface, a 25% overlap between the successive melt tracks was followed. The angle between the powder nozzle and the specimen was maintained at 50 degree. The shrouding Ar gas flow rate was maintained constant at 6 l/min. Following laser surface modification, the microstructure of the modified layer (both the top surface and the cross-section) was characterized by optical and scanning electron microscope. Microhardness of the top surface and along the cross-sectional plane of the surface were measured by a Vickers micro hardness tester. Finally, the kinetics of wear of the surface modified MEZ was compared with the as received one by a Pin-on-Disc wear testing machine against hardened steel disc with a 3-kg applied load and300-rpm wheel speed
b) Results of Experiment:
In laser surface modification, Al melts to form an alloy with Mg matrix and hard Al2O3 particles get instantaneously distributed throughout the molten zone during laser surface melting operation to form the composite layer distributed in alloyed zone of Mg and Al. Due to a large difference in density between the particles and matrix and differential absorptivity between the Al+Al2O3 particles and MEZ, choice of suitable process parameters is crucial to achieve a uniform intermixing and proper penetration of the alloying element and hard particle in the surface modified layers. An adherent and defect free interface with negligible heat affected zone may be noted. The microstructure of the surface layer mainly consists of dispersion of Al2O3 particles in the hypo-eutectic matrix of Mg and Al. The morphology of the alloyed zone is predominantly dendrites of primary magnesium with eutectic lamellae of Mg17Al12 and Mg in the inter dendritic spacing. The interface is defect-free and microstructure of the interface is mainly dendritic in nature.

![Image](a)

![Image](b)

![Image](c)

**Figure 2** Scanning electron micrograph of the (a) cross-section showing composite surface and substrate, (b) top surface and (c) composite surface–substrate interface of laser surface modified MEZ with Al+Al2O3.

There is presence of mainly, Mg17Al12 and Al2O3 peaks along with Mg and a few unidentified peaks of compounds of Mg and RE elements (as present in as-received MEZ) and compound of Al and RE element. The X-ray diffraction profile conforms to the microstructure of the surface modified layer. The microhardness of the laser surface modified MEZ with AlqAl2O3 was measured both on the polished top surface and along the cross-sectional plane as a function of laser power and scan speed. The average micro hardness of the surface modified layer was significantly increased as compared to as-received MEZ. The average microhardness of the surface layer of the composite surfaced specimen decreases with increase in laser power. Average microhardness of the surface layer decreases with increase in scan speed, because of decreased particle input as a result of lowering of interaction time associated with a higher scan speed.
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The wear loss of as-received and laser composite surface MEZ were measured by a Pin-on-Disc wear testing machine against hardened steel disc, subsequently measuring the wear loss of materials at a regular interval. It was noted that wear loss is considerably reduced due to laser surface modification. The superior wear behaviour of laser surface modified layer is attributed to improved Micro hardness in the surface layer because of the presence of hard ceramic particles and alloying with aluminium.

c) Conclusion:

- The microstructure of the surface modified layer consists of dispersion of Al2O3 particles in the hypoeutectic matrix of Mg and Al. The morphology of the alloyed zone is predominantly dendrites of primary magnesium with eutectic lamellae of Mg17Al12 and Mg in the interdendritic spacing.
- A detailed X-ray diffraction analysis shows the presence of mainly, Mg17Al12 and Al2O3 peaks along with Mg and a few unidentified peaks of compounds of Mg and RE elements (as present in as-received MEZ) or compound of Al and RE element in the surface modified layer.
The microhardness of the surface modified layer was significantly improved to as high as 350 VHN as compared to 35 VHN of the substrate value. The average microhardness was, however, found to decrease with both the laser power and scan speed.

Wear resistance was significantly enhanced due to laser surface modification. The superior wear behaviour of laser surface modified layer is attributed to improved microhardness in the surface layer because of the presence of hard ceramic particles and alloying with aluminium in surfaced MEZ as compared to as-received one.

4. ELECTROLESS NICKEL PLATING ON AZ91D:

a) Experimental details:
The substrate material used for the present investigation was AZ91D ingot-cast alloy. Rectangular coupons of size 20*40*4 mm were used for the investigation. The surface of the substrate material was wet-ground (using water) on 1000 grade SiC paper and polished on a diamond wheel using 6-mm diamond paste. The polished specimens were thoroughly washed with water before passing through the pre-cleaning. Immediately after the fluoride activation (last step in the pre-cleaning process), the specimen was quickly transferred to the coating bath. A fresh bath was used for each experiment to avoid any change in concentration of bath species.

The specimens were coated for the required length of time, removed from the bath, washed with water and acetone and air-dried. Final weight of the specimen was determined and the coating rate in mm/hr was calculated from the weight gain. In this work, the initial weight of the specimen was measured prior to pre-cleaning steps. The coated specimens were characterised to evaluate the coating performance. Coating morphology was analysed using optical and scanning electron microscope.

EDX analysis was used for the determination of phosphorus. Microhardness measurements were carried out using Shimadzu hardness testing machine using a load of 100 g. The structure of the deposit was determined using X-ray diffraction technique.

b) Results of Experiment:
The microstructure consisted of primary a, eutectic a & b-phase. The b phase is an intermetallic with the stoichiometric composition of Mg17Al12. Coring during solidification resulted in considerable variation in the distribution of aluminium and zinc in the microstructure of AZ91D alloy.

The coating thickness was directly proportional to the plating time. In the present investigation, coating formed in optimised bath composition was found to be amorphous possibly with microcrystalline areas. The phosphorus content showed a sinusoidal variation with average phosphorus content decreasing from interior to exterior. The alternate layers contain high amount of phosphorus with layers in between exhibiting lower values. The average phosphorus content in the deposit was 7–8 wt% with a hardness value ranging between 650 and 750 VHN depending on the plating parameters.
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![Graph](image1)

Figure 4 Structure of electro less nickel-coating on AZ91 substrate after 4 hrs. (a) diffractogram, (b) cross-section of the coating showing lamellar structure and (c) phosphorus content across the lamellar structure

Although the alkaline cleaning did not etch the surface, the surface after chrome–nitric pickling and fluoride activation was etched, so that the different micro constituents could be clearly seen. After hydrofluoric acid cleaning, the surface was found to be smooth and flat, where flat b phases can be seen as dark phases. The less dark regions adjacent to b-phase is the eutectic a-phase containing a higher amount of aluminium. Electroless nickel nucleated on the AZ91D substrate at different intervals of time. The coating has been preferentially nucleated on b-phase, which then spread to eutectic a and primary a-phase. The coating on primary a-phase was formed as a continuation of the deposit on b-phase and eutectic a phase, after the b-phase and eutectic a-phase was covered with coating. However, the coating on the b-phase was discontinuous and grew slowly, which led to a concentration of defects over this region. From the EDX analysis of the early stage deposits on b-phase at different intervals of time showed slightly lower amounts of phosphorus content, which increased simultaneously with coating growth. However, this phenomenon was observed in a very thin layer of coating at the surface while on the average. Areas of the coating attached to eutectic a-phase showed a higher amount of Mg than the primary a-phase.

Both the pre-cleaning steps and the concentration of bath constituents have an influence on electroless nickel coating. The fluoride ion is an essential component for electroless nickel-plating bath for magnesium, and its presence in the bath was reported to improve adhesion. Variation of coating rate, phosphorus content and hardness with concentration of ammonium bifluoride in the coating bath. Electrochemically b-phase is reported to be more cathodic.
(more noble) to eutectic a and primary. The lower aluminium containing primary a-phase is expected to have most active (more negative) potential in magnesium alloy. Possible explanation is that the initial stage of deposition has been influenced by a galvanic coupling between b-phase and adjacent eutectic a-phase. The electrons produced by the anodic dissolution of magnesium from the a-phase are consumed by the cathodic deposition of Electroless nickel on b-phase. The presence of Mg (OH) 2 over eutectic a-phase and less phosphorus in early nickel deposits might support this argument. The lamellar structure of the deposit has been attributed to the compositional variation of phosphorus within the deposit. The overall decrease in phosphorus content with coating thickness might be attributed to the reduction in the concentration of hypophosphite as coating proceeds.

![Figure 5](image)

**Figure 5** Effect of ammonium bifluoride on the morphology of the coating on AZ91: (a) 7.5 g/l and (b) without fluoride.

To activate the magnesium surface, fluoride was added in the form of hydrofluoric acid and ammonium bifluoride, which also increases the adhesion of the coating. The presence of citric acid and ammonium bifluoride also serves the purpose of buffers and accelerators. The autocatalytic electroless nickel deposition was initiated by catalytic dehydrogenation of the reducing agent with the release of hydride ion, which then supplied electrons for the reduction of nickel ion. The role of the complexing agent on electroless nickel-coating on AZ91 alloy can be explained on the basis of three aspects i.e. (a) a reduction in the concentration of free nickel ions, (b) preventing the precipitation of basic nickel salts and nickel phosphate, and (c) exerting a buffering action. The initial dip in hydrofluoric acid activates the substrate surface, and forms a fluoride film over the surface.

c) Conclusion:

- The electroless nickel-coating deposited on AZ91D alloy in optimised bath showed amorphous structure with 7 wt.% P and a hardness value of 600–700VHN. The microstructure of the coating in the transverse direction showed lamellar structure with a phosphorus content varying in a sinusoidal manner.
- A strong influence of substrate microstructure was found. Initially, the coating was nucleated preferentially on b-phase. The coating spread over to primary a-phase, once the b-phase and eutectic a-phases were covered with electroless nickel.
- Optimum ligand–nickel ratio was found to be 0.33(Ligand:Ni2q(1:3), whereas the best concentration of thiourea was 1 mg/l. Fluoride ions were essential to plate electroless nickel on AZ91D alloy with an optimum concentration of 7.5 g/l of ammonium bifluoride.
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- The presence of 0.5 mg/l of MBT in the plating bath doubled the plating rate. However, for a stable bath, the optimum concentration of thiourea and MBT was 0.5 mg/l of former with 0.25 mg/l of the latter.

5. NANOPARTICLES BASED INORGANIC COATINGS ON MAGNESIUM ALLOYS:

a) Experimental details:
Aqueous coating sols used are prepared from commercial dispersions and H3BO3, Na2B4O7, NaH2PO4, Na2HPO4, NaOH, KOH, Al(OH)3 dissolved in distilled water. If necessary the pH value can be adjusted to 8–9 with nitric acid. Mixed silicon, phosphorus and boron oxide nanoparticles for electrophoretic deposition are prepared from tetra ethoxysilane (TEOS), triethyl borate and triethyl phosphate from ethanol and ammonium hydroxide as catalyst. The substrates to be coated were first of all ground (SiC paper from P1200 to P4000) and degreased in caustic and acetone. For AZ31 a further acidic activation with Nital (2%HNO3 in ethyl alcohol, 5 s) resulted in the best wetting behaviour by water based solutions. AZ91 could best be prepared by a treatment with 2%HNO3 in glycol/H2O (75: 25).

For coating application these prepared samples were either dipped into the coating sol and withdrawn at constant speed (1 cm min−1) or whisked in one draw with a brush wetted in the coating sol. Because of possible water electrolysis the EPD was performed from ethanol based dispersions. However, up to 10% water content can be tolerated to increase dispersion stability and conductivity. The magnesium sample to be coated was therefore switched as the anode. At a solid content of 2% or less and a constant voltage of up to 5 V coating deposition was performed in up to 30 min. All samples were dried at room temperature and afterwards sintered in synthetic air.

b) Results of Experiment:
The coating sol may be applied to the cleaned and activated substrate by dipping or brushing. For dipping the coating thickness is dependent on the viscosity of the sol as well as on the speed of withdrawing the sample from the sol. If pulled out slowly, coatings will be verythin.8 as magnesium alloys are not stable under acidic conditions sol stabilisation at low pH is not possible. Because shrinkage of the coatings during drying and densification is limited to only one dimension the maximum coating thickness is strongly limited. For pure inorganic SiO2 films the critical thickness without cracking is mostly below 1 mm. Further complicating is the great difference of the thermal expansion coefficients between magnesium and the silicate layer. This leads to additional stresses during sintering and therefore to cracking or delamination. Nanoparticles may, however, increase the critical coating thickness.11,12 Suitable additives can be used to adjust the thermal expansion coefficient of the coating to the substrate and this way to avoid cracking. A further possibility to decrease the stresses in the cross-linked coating and to make them more flexible is the use of network modifiers.

Dip coated layers tend to become thicker than brushed coatings under the same conditions and therefore have a higher tendency to form cracks within the layer. However, with both methods it is possible to obtain thin, crack free layers with a thickness below 1 mm.
An alternative route of coating application is the use of electrophoretic deposition (EPD). This method is based on the fact that in dispersions under an applied electric field, particles will move towards the oppositely charged electrode and will coagulate there. By this method coatings with high green density may be obtained also from dispersions with low solid content. However, only solids will be deposited. Therefore all sintering additives must be contained in the particles. The obtained coating thickness is dependent on concentration, time, voltage and applied current. A further advantage of EPD is that coatings may also be applied to surfaces with complex geometries. Electrophoretic deposition has been performed with silicon dioxide based particles which also contain boron and phosphorus oxide made by the sol–gel process. For this purpose particulate sols were directly used, or isolated oxide particles were redispersed. Especially at the beginning of the deposition process a strong decrease in the current can be observed. This shows that the anode surface is covered by isolating nanoparticles. The amount of particles deposited per time decreases with the current flowing. Longer deposition times do not lead to a significantly higher coating thickness.

Despite the high green density possible with this method, thicker coatings also tend to form cracks. After sintering crack free coatings could only be obtained below 2 mm so far. Electrophoretic deposition coatings without further additives consisting of 35 nm particles show some micro cracks and an average roughness of 15\(\mu\)m after the sintering process. Thick layers can be obtained by the use of large particles, but close packing of larger particles also results in lower density and therefore higher shrinkage during sintering than that of smaller particles. In a two step process a thick layer of a first EPD can be formed by large particles. The wide gaps between the large particles could be filled by a following second deposition of smaller particles.

c) Conclusion:

- By dip coating, brushing and electrophoretic deposition thin transparent and crack free coatings based on nanoparticles could be applied onto the magnesium alloys AZ31 and AZ91. Sufficient densification of the coatings was already possible at moderate temperatures. Especially aluminium containing coatings show good properties after a heat treatment at 200\(^\circ\)C, which should avoid any damaging of the magnesium substrate.
- The coating thickness, especially for dip coating and brushing is still quite low and should be increased to guarantee a good corrosion performance.
- The dispersions and additives to be used are less expensive than the alkoxides used in the classical sol–gel process. Hence the use of commercial products further increases the value of this new method especially for industrial applications.
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ACKNOWLEDGEMENT
We gratefully acknowledge department of Automobile Engineering of Pimpri Chinchwad, Polytechnic, Pune (India), for technical support and providing the research facilities. Their help and dedication toward our work and related research, also their library staff and expert for their directly and indirectly help, support and excellent co-operation.

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