

Journal of Synergetic Research and Technology

<http://www.jsrt.in>

Review Article

SURFACE MODIFICATION OF MAGNESIUM ALLOYS FOR BIOMEDICAL APPLICATIONS- A REVIEW

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Abstract

Magnesium alloy considered as a most suitable biodegradable material in biomedical field and fundamental research in terms of finding fresh clinical applications and products. Magnesium (Mg) alloy used as a implantation material in human body exclusively for bone fractures. At the same time, fast degradation of Mg alloy was identified as most challenging factor in implantation and it creates mechanical loss. Due to this drawback, surface modification on Mg surface is identified as a suitable solution to reduce fast degradation. This surface modification leads to avoid fast degradation, gap formation on bio implants and tissues in human body. Surface modification techniques and its importance on Mg alloy have a huge potential and research scope. This chapter is exploring about detailed study on Mg surface modification techniques such as electro deposition, friction stir processing, anti-corrosion coating etc.

Keywords: Magnesium alloy, Surface modification, Electro plating, Anti-corrosion, FSP.

Published: 25-03-2026

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1. INTRODUCTION

Polymers and ceramics are not as potentially used as implant material due to lack of strength and stability. The metals like titanium, steel and other chromium-based alloys are dominant bio implants compare to ceramics and polymeric materials [1]. Due to high mechanical properties, metallic material completely dominates the bio medical field. However, metallic materials used as temporary implants in bones and other treatments. In such causes, second surgery is necessary to remove the implants from human body. It provides the complication to the body hence it is necessary to identify another material which is almost required to the human body. Additional advantages of this new material are to avoid the second surgical operation for implants removal after the tissue is completely restored [2]. Figure 1 represents the limitations of traditional material used in implantation and fracture treatment.

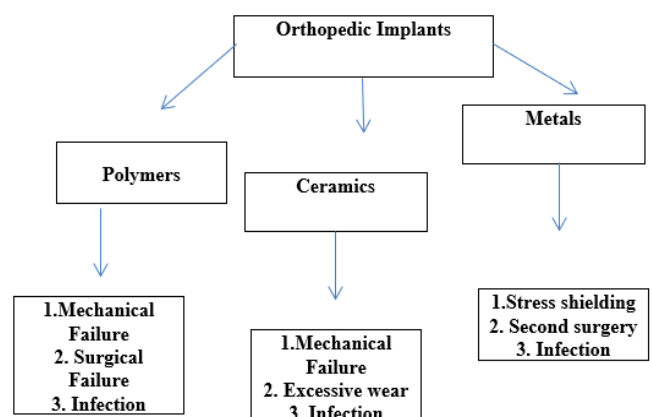


Figure 1: Limitations of traditional materials

Magnesium alloy (Mg) and Iron (Fe) both are considered as suitable degradable material in recent days. But Mg alloy degrades in faster rate in human body compare to Fe. At the same time, Fe was identified as very slow degradable material as bio implants. Both bio degradable rates are not acceptable for bio implants. Hence study of surface modification and its techniques is highly required [3]. Mg alloy attracted high to the researcher in recent days due to similar mechanical property when it is comparing to human bone and density (1.74 g/cm^3). Mg is considered as most wanted nutrient to maintain healthy and growth of human bones [4]. Mg alloy also have some limitations such as corrosion in fluidic environment due to high chemical galvanic corrosion nature. But still Mg is proven as nontoxic material in biomedical applications. Recent research work on Mg alloy made several efforts to enhance the mechanical and anti-degradation efforts on Mg alloy. These efforts are classified as metallurgical modification or surface modification of Mg. Surface modification generally enhances the mechanical integrity, biocompatibility and degradable nature by turning Mg microstructure [5]. Different magnesium alloy is available namely AZ31, AZ31, AM60 and LAE442. For surface modifications in Mg alloy, electro plating, friction stir processing, chemical conversion technique are commonly used [6]. Suitable surface modification on Mg was picked based on applications. Laser surface modification also termed as promising technique widely considered in recent days. The advantages and disadvantages of Mg for bio medical applications are given in table.1. This chapter explores with surface modification techniques for Mg alloy, advantages and disadvantages.

Table 1: Advantages and disadvantages of Mg for bio medical applications

S. No.	Advantages	Limitations	Key Findings
1	Low Density	Rate of degradation	Density related to human bones
2	Minimum Elastic Modulys	Hydrogen evaluation	Hydrogen evaluation induces high degradation
3	Degradability	Low clinical strength	Fast degradation leads to lake of in heal and tissue formation
4	Good Machinability	-	Stable dimension is possible
5	High specific strength	-	260 kNm per kg.

2. SURFACE MODIFICATION TECHNIQUES

2.1. ELECTROPLATING

The process of forming thin metal coating on electrode by using electric current is called as electroplating. Here electric current is used to decrease the dissolved metal cautions for

forming thin coating on an electrode. In other words, deposition or coating of one metal in to other with the help of salt solution or aqueous solution is known as electroplating. The principle of electroplating and its suitable sketch is shown in Figure 2.

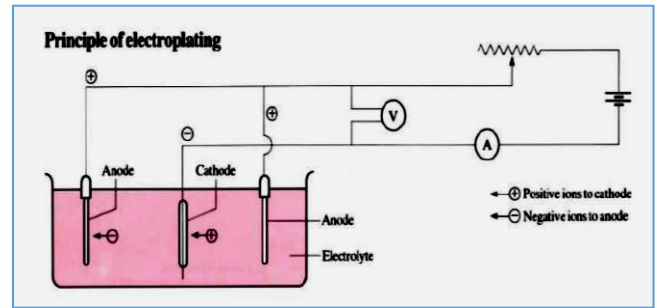


Figure 2: Principle of Electroplating [7]

In electroplating method, two electrodes are used namely anode and cathode. The positive charge is called as anode and negative electrode is cathode. Bothe anode and cathode is placed in a closed container with electrolyte. Under electric supply, positive ions attracted by cathode and metal coating takes places. Viswanathan et al. [7] used Magnesium AZ31B alloy for surface modification. Magnesium alloy is considered as base metal and the chromium is considered as coating substrate. Due to high corrosion resistance, chromium coating on AZ31B was planned and executed. They stated that, chromium coating on AZ31B alloy improved the hardness of the base metal by 53BHN (Brinell hardness number) from 49(BHN). Also, they stated that, foam like electro deposition was formed on the base metal and came out of base metal. Chromium layer was not completely formed due to inadequate precautions. This is due to high galvanic corrosion of AZ31B. To overcome this issue Chen et al. [8] has already mentioned a detailed steps on electroplating as given below. (Figure 3)

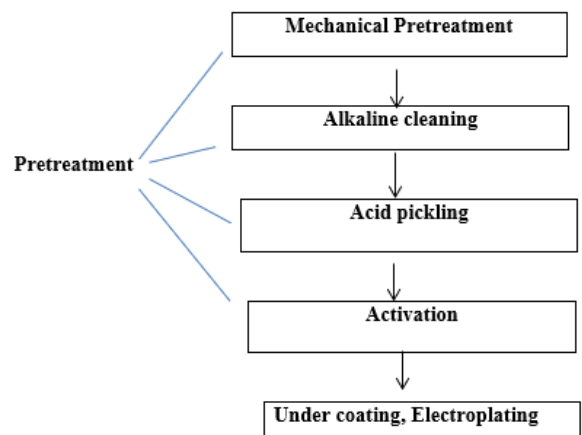


Figure 3: Steps in Electroplating

In pretreatment process, it is classified into four major steps namely mechanical pretreatment, cleaning in alkaline, acid pickling and activation. To minimize the galvanic corrosion of magnesium alloy, under coating is highly

necessary before final electroplating of the metal. Adhesion nature is also increased due to under coating technique. For under coating, Zinc immersion electroplating is preferred. The use of pretreatment process is presented in table 2.

Table 2: Application of pretreatment process

S. No.	Method of Pretreatment	Application
1	Mechanical method under grinding, polishing and particle blasting	Oxide, dirt and burred edge removal
2	Alkaline cleaning (NaOH 50g/l 10 to 15 min at 65 degree)	Grease, Oil and organic matter removal
3	Acid Pickling with CrO ₃ 180g/l with time limit of 1 to 15 min at 100 degree	Flux, corroded particle
4	Activation (HF for 5 to 10 min)	Direct electro less plating.

Zhang et al. [9] has done an aluminum electroplating on AZ31 alloy. They stated that, acetic anhydride was used to immerse the magnesium AZ31 alloy as a pretreatment process which is used to reduce the formation of oxide over the base metal. It is due formation of magnesium acetate layer on the metal surface. They also stated that, aluminum deposition over the AZ31 alloy provided crack free surface and it improved the corrosion resistance. At the same time, hardness is noted as 2.7GPa.

2.2. FRICTION STIR PROCESSING

Friction stir processing (FSP) is a surface modification technique evolved from friction stir welding process. FSP consist of non-consumable tool used to create heat and plastic deformation of base metal. This severe plastic deformation which is done by friction tool induces the homogeneous surface modification and fine-grained microstructure. The suitable sketch for FSP and its principle is shown in Figure 4.

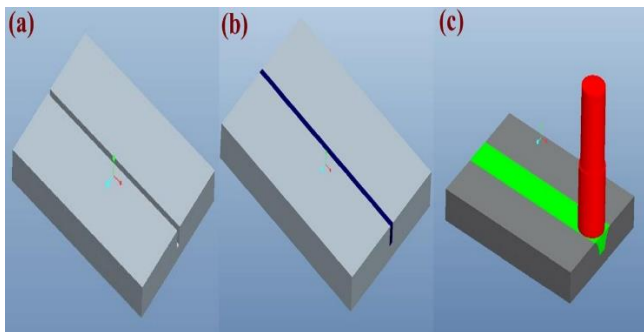


Figure 4: FSP: (a) Making groove, (b) Reinforcement filling and (c) Friction tool pass

In FSP, reinforcement particle is filled on the groove for surface modification is stirred with tool which induces high heat and plastic deformation. The high-speed tool moves in work axis and advanced over the tool work surface. Due to

friction, enormous amount of heat is produced on the work surface and plastic deformation takes place in the processed zone. This principle results the surface modification on the base material. Generally, it is done in single tool pass technique. In recent days, multi pass technique enhances the surface quality, material dispersion and formation of fine grains. Multi pass FSP technique is presented in Figure 5. In multi pass technique, pin type and non-pin type of friction tool is used to do surface modification.

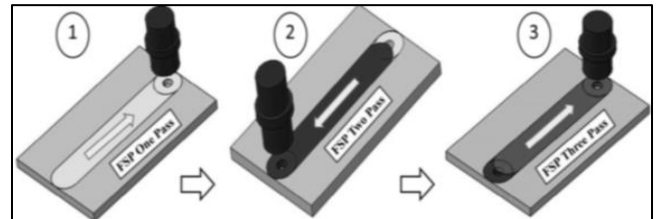


Figure 5: Multi Pass FSP Principle [10]

Darras et al [11] performed Friction stir processing on AZ31B using single pass technique. The entire work was done with 2000 rpm and 30inch per min traverse speed of tool. They found that, refined grain size was achieved from 6 to 3 micro meter and hardness of Mg alloy was increased from 68 HV to 72HV in the processed zone. Hütter et al. [12] performed surface modification in AZ91 and pure magnesium. They found that, corrosion resistance and hardness is significantly improved when it is compared to base work. The advantages of FSP in surface modification are given in table 3.

Table 3: Advantages of FSP in Mg surface modification [13-15]

S. No.	Base Material with tool	Advantages
1	AZ31 with steel tool	Grain size enhancement and super plasticity
2	AZ61 with steel tool	Grain refinement upto 7.8µm in multipass FSP
3	AZ91 with HCHC steel tool	High hardness and corrosion resistance
4	AZ31B with steel friction tool	Less thermal boundaries and controlled grains
5	AZ61 with steel tool two pass	Enhanced microstructure evolution

Surface Modification using FSP provides better bioactivity of metallic implants generally Upgraded degradation performance of metallic implants.

2.3. LASER SURFACE MODIFICATION

Laser surface modification is a thermal process on the material which is having a traditional improvement over conventional method. It is also called as laser surface texturing (LST). LST is defined as the process of changing properties of material surface by changing its texture of material surface and its roughness. The laser beam is used to

produce the micro patterns over the surface of base material. The principle of Laser surface modification is given in Figure 6.

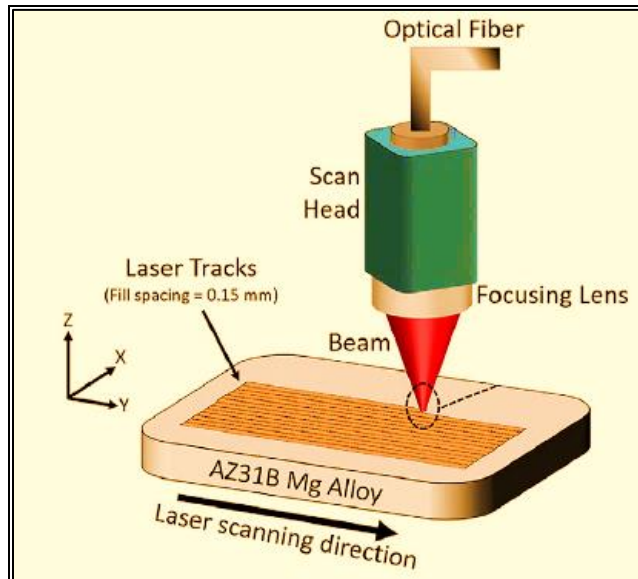


Figure 6: Principal of Laser surface modification

Ma et al. [16] reported that, laser surface modification technique provided high surface integrity, high quality with minimum cost. Also, it provided most efficient anti-corrosion on magnesium alloy when compared with chemical and physical surface modification methods. Ma et al. also performed the surface modification over Mg-6Gd-0.6Ca alloy with continuous wave laser. The wavelength of this fiber is 1060nm with spot size of 100 μm . The Mg alloy surface was exposed with laser density of power as $2.04 \times 10^6 \text{ W/cm}^2$ and 70mm/s of scanning speed with argon protection. At the end of the surface modification, galvanic corrosion of Mg was reduced and thickness of layer produced by the laser is 360 μm . Florian et al. [17] stated that, high corrosion resistance and bio wettability was achieved on Mg surface modification using laser treatment. Rakesh et al. [18] prepared Mg-Zn-Gd alloy block it is converted into smaller pieces with the dimension of 100 mm $\times$ 30 mm $\times$ 8 mm and surface dimension of 90 mm $\times$ 20 mm area for laser surface melting (LSM). Ytterbium doped continuous wave fiber laser was used to perform laser melting with beam diameter 500 μm . 1mm below of Mg alloy surface was selected as focal position with 225W laser power and 20mm/s scan velocity. At the end of experiments, improved wettability was achieved with surface energy $40 \pm 5 \text{ mN/m}$.

2.4. DIP AND SPIN COATING

Dip coating is a simple method which includes material deposition on wet liquid with the help of substrate immersion in to coating solution. Immersed material should be removed with constant speed in the atmospheric temperature. The suitable sketch of dip coating is shown in Figure 7. Spin coating is another simple method of material surface modification and it is represented in Figure 8.

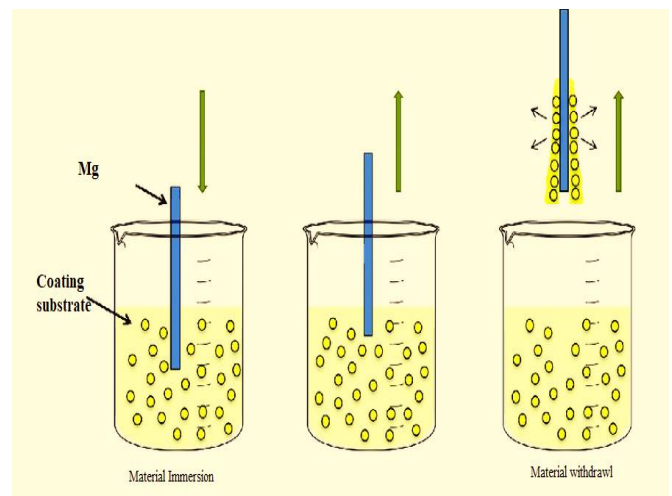


Figure 7: Dip coating

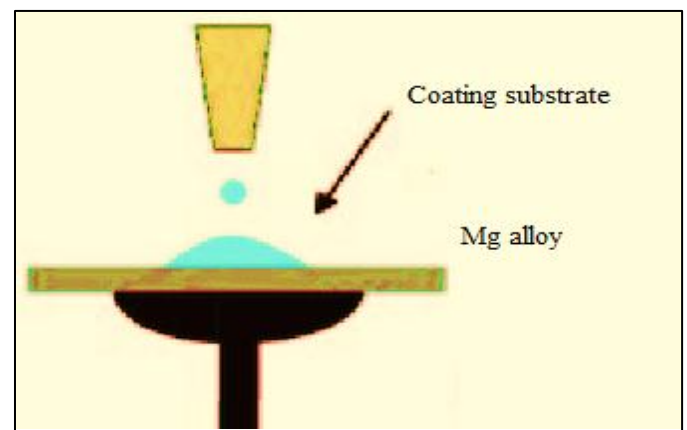


Figure 8: Spin coating

In spin coating, spinner is used to fill the coating film over the base metal with uniform thickness. This is done by centrifugal force created by the spinner. Advantages of Laser surface modification and other methods are given in table 4. Thiago et al. [19] produced anti-corrosion layer on Mg alloy with spin coating process. 2 * 2 cm of Mg sample was used to perform material surface modification. The spinning velocity of 1600rpm was adopted for 100s and 3ml of polymer was used as a coating agent. 150s of dry time was given to ensure dryness of the coating element. The experimental results showed that, 2 μm thickness showed the better corrosion resistance with coating agent of 15 wt.% solution in N,N'-dimethylacetamide. The advantages of surface modification are given in table 4.

Table 4: Advantages of surface Modification

S. No.	Surface modification method	Advantages
1	Laser Surface modification	1.Improved corrosion resistance 2. Enhance mechanical and wear properties 3. high degradation resistance
2	Electrodeposition	High biocompatibility and degradation resistance
3	Dip coating	Minimum cost, uniform coating and high degradation resistance
4	Spin coating	Minimum cost, uniform coating and high degradation resistance
5	Thermal spray	High material deposition and coating thickness
6	Anodization	High degradation resistance

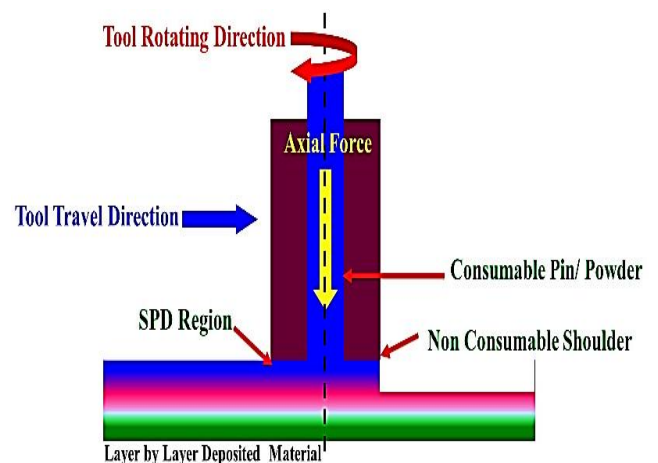
2.5. FRICTION-SURFACING

Friction surfacing (FS) is a solid-state method using localized surface medication technique and it is presented in Figure 9. The FS has been performed the fine-grained coatings, which exhibit superior wear and corrosion properties. Several studies also emphasize its energy efficiency and low environmental impact as key advantages when compared with other alternative technologies. Main applications include repair of worn or damaged surfaces through building up or crack sealing. A wide range of material combinations have been deposited by FS, mainly alloy and magnesium, Aluminium, and titanium alloys have also been investigated, including the production of metal matrix composites [20]. Frictional contact is imposed on the interface against a molecule due to the axial load applied. As a result, a layer formed between underneath of tool and substrate, from this process inter diffusion mechanism at high temperature and pressure to form metallurgical bonding [21]. The layer formation is easily controlled by the forging pressure of axial direction, traveling feed of consumable tool and speed of the tool. The parameter can be optimized which increases the quality of friction deposition [22,23]. The initial applications of the technique were to coat the surface of various metals with the uniform of fine grains coating for better wear and corrosion resistance. After being applied the deposition of the materials into hardened phases that cannot be filled by other fusion methods is extended to the hard surface. This original frictional surface concept in new developments may however be used in solid state coating. [24].

Magnesium alloys have been vital applications as metallic biodegradable materials for medical applications. The biomedical application material of Magnesium alloys is addressed the deposition of AZ91 casting bars over AZ31 magnesium plates. In this process has no mechanically mixed layer was formed between the deposit and the substrate. Typical use of magnesium substrates never permits the penetration of steel, aluminium, titanium and copper. Contact pressure and heat resulted in the plasticization of the magnesium substrate instead of the consumable rod tip.

2.6. MICROSTRUCTURE

FS are characterized by the interesting microstructural features due to the variation in thermal behaviour of the layer-by-layer development of 3D size from bottom to top direction. The material flow is easily regimented by the tool geometry and tool parameter during the process. Hence, the microstructural properties are varied at different layers during processes. In the process, first layer is placed over the substrate of material. FS is better microstructural altered due to the severe plastic deformation of the material and dynamic recrystallization. Palanivel et al resulted that multi layered of an Mg based WE43 alloy was fabricated by using FS at two different parameters. In this process, heat input is made formation of sensitive defects and dynamic recrystallisation controlled the fine grains of 2–3 μm [25]. The fine grains are led to superior mechanical properties. Changshu et al. discussed that microstructural evolution of multilayer 4-mm thick 7N01-T4 Al alloy sheets using FS. The layer is observed the Hook and kissing bond defects. The hook defect is formed by non-bonding interfacing of metals and kissing bond is lacking of material flow. Avoid such defects can be increased the forging force or pressure of the tool and speed of tool [26].

**Figure 9:** Friction-surfacing process.

2.7. Shot Peening process

Shot peening is one of the surface modification methods represents cold working process mainly utilized to impart compressive residual stresses over the work surface, which gives mechanical properties modification. This is used to

enhance strength and diminish the stress profile of the base metal. The suitable shop peening sketch is given in Figure 10.

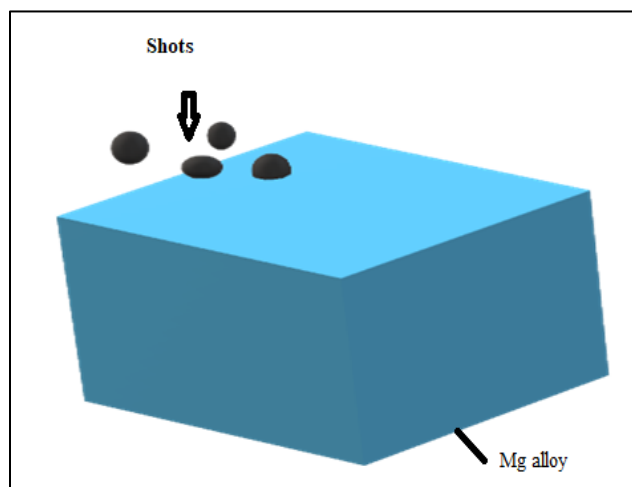


Figure 10: Shot peening process

Peral et al. [27] studied the plastic deformation on the top layer of magnesium alloy AZ31 alloy due to change the surface properties of magnesium alloy and reduce the surface corrosion damages. Severe traditional shot peening was done over AZ31 alloy with room temperature, above and below recrystallization temperature. 240 °C and 360 °C are considered as above and below recrystallization temperature. They studied about grain refinement, hardness of the surface and stress and surface roughness. They found and ensured the corrosion resistance was improved along with surface roughness. Change in grain size also possible in shot peening process.

3. CONCLUSION

Magnesium alloy is the most commonly used light metals for biomedical applications. Due to high galvanic corrosion and degradation rate, surface modification of magnesium alloy is much needed. Based on the detailed study, the following points were concluded.

1. For surface modification, friction processing, friction surfacing, electroplating, shop peening was commonly used.
2. Surface modification mainly focused to improve the surface hardness, corrosion resistance and minimize the degradation rate.
3. For bio medical applications, surface modification was performed to improve the strength of the Mg alloy and mechanical properties.
4. Machining, machinability study and corrosion resistance will be a future scope of Mg alloy for biomedical applications.

CONSENT FOR PUBLICATON

None Declare

CONFLICT OF INTEREST

None Declare

ACKNOWLEDGEMENT

The authors express their gratitude to Kongunadu college of Engineering and Technology for support.

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