

Advanced Compound Coating for Delaying Corrosion of Fast-Dissolving Alloy in High Temperature and Corrosive Environment

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Abstract—Fast dissolving magnesium (DM) alloy technology has contributed significantly to the “Shale Revolution” in oil and gas industry. This application requires DM downhole tools dissolving initially at a slow rate, rapidly accelerating to a high rate after certain period of operation time (typically 8 h to 2 days), a contradicting requirement that can hardly be addressed by traditional Mg alloying or processing itself. Premature disintegration has been broadly reported in downhole DM tool from field trials. To address this issue, “temporary” thin polymers of various formulations are currently coated onto DM surface to delay its initial dissolving. Due to conveying parts, harsh downhole condition, and high dissolving rate of the base material, the current delay coatings relying on pure polymers are found to perform well only at low temperature (typical < 100 °C) and parts without sharp edges or corners, as severe geometries prevent high quality thin film coatings from forming effectively. In this study, a coating technology combining Plasma Electrolytic Oxide (PEO) coatings with advanced thin film deposition has been developed, which can delay DM complex parts (with sharp corners) in corrosive fluid at 150 °C for over 2 days. Synergistic effects between porous hard PEO coating and chemical inert elastic-polymer sealing leads to its delaying dissolution improvement, and strong chemical/physical bonding between these two layers has been found to play essential role. Microstructure of this advanced coating and compatibility between PEO and various polymer selections has been thoroughly investigated and a model is also proposed to explain its delaying performance. This study could not only benefit oil and gas industry to unplug their High Temperature High Pressure (HTHP) unconventional resources inaccessible before, but also potentially provides a technical route for other industries (e.g., bio-medical, automobile, aerospace) where primer anti-corrosive protection on light Mg alloy is highly demanded.

Keywords—Dissolvable magnesium, coating, plasma electrolytic oxide, sealer.

I. INTRODUCTION

TWO decades of the Shale Revolution has transformed the global energy market [1], in part by the adaption of multi-stage dissolvable frac plugs. These plugs block the well temporarily during hydraulic fracturing operation, and quickly “disappear” afterwards via dissolving in produced fluids from reservoir [2]. Advanced magnesium alloys, favored for plugs fabrication, have micro-galvanic cells built into their microstructures and disintegrate through galvanic corrosion [1], [2]. Various grades of these alloys, different in mechanical properties and dissolving rate, have been customized and commercialized to fit specific well conditions. Among those

applications, high temperature high pressure well with downhole temperature above 150 °C is proven to be most challenging, because mechanical properties of Mg alloy deteriorate rapidly at elevated temperatures (> 120 °C) and their reactivity with downhole fluids also increased exponentially with temperature increase [3]. Therefore, it has been frontier of DM research to achieve Mg alloy with controlled dissolving rate and reasonable mechanical property above 150 °C. So far, various new elements (e.g., rare earth [4], [5]) and technologies (e.g., ceramic-metal composite [6]) have been utilized, and some of them are even successfully commercialized given various issues that still needs to be addressed.

During operation, degradable plugs are required to keep mechanical integrating under high stress during hydraulic fracturing process in the first 6-24 h (depending on operation design), and need to be dissolved as quick as possible without large solid residual, not only to put wells into production quickly, but most importantly to prevent wrapping of downhole oil and proppants. This wrapping is reported to isolate DM from water and stop DM dissolving process completely, leading to permanent blocking of wells [7]. The former requirement demands DM to have lower dissolving rate so that plug can maintain reliable strength during operation, while latter requires DM to have dissolving rate as high as possible. A conflicting requirement leads to two kinds of broadly observed failure in field, either “premature” disintegration or not dissolving at all at the end [7]. To address this issue, delayed surface coating (or “temporary coating”), such as polymer spray coating, has been utilized on a fast dissolving DM to delay its initial dissolving process [8]. However, these coating are found mainly successful to protect very simple geometry (e.g., ball shape), and all fails at high temperature (> 120 °C) due to either degradation of coating material itself or delamination of coating from base metal. It is true that polymer coating and other coatings, e.g., E-plating, chemical conversion, electrochemical plating, Plasma Electrolytic Oxidation (PEO), etc. [9], [10], have been proven successful in automobile industry, however, these coatings are found either too thick for plug parts (i.e., exceed design tolerance) or incompatible with downhole fluids based on our tests. There are also some precision coating technologies (such as PVD, CVD, etc. [11], [12]) reported promising in lab, however, most of them cannot be scaled up economically in oil and gas industry. For this sake, it is in great demand to develop effective and cost-efficient delay coating with HT rating > 150 °C so as to unlock vast amount of HTHP shale reservoirs inaccessible

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In this study, we examined failure mode of various industrial coating technology at elevated temperature, and address their issues via developing a coating system-PEO combined with elastic HT sealer. This coating successfully delays DM dissolving process for more than 2 days at 150 °C, maximum required for oil field application. To best of our knowledge, this is first industrial report to achieve thin delay coating for complex DM parts over 140 °C for oil and gas industry. Microstructure of this coating was also analyzed and a mode has been proposed to explain the synergistic effects between porous hard PEO coating and chemical inert elastic-polymer sealing.

II. MATERIALS AND EXPERIMENT

In order to understand detailed degrading process of various coatings, AZ31 Mg alloy with slow dissolving rate was selected as base metal. Cuboid shape with dimensions (6 mm × 25 mm × 76 mm) was machined directly from a HT extruded AZ31 bar as samples for coating, and its 8 sharp corner and edges represent the most severe scenarios that could occur to DM parts used in degradable plugs. For polymer spray coating, AZ31 cuboid sample was first rinsed with organic solvent to remove surface oil residue, its surface was then treated with sand-blasting, activated with primer, and industrial grade polymers were finally spray-coated with various thickness according material specification. Various polymers have been tested in this study, including epoxy, ethylene chlorotrifluoroethylene (ECTFE), Polyphenylene sulfide (PPS), Polyether ether ketone (PEEK), etc. For PEO plus sealer coatings, cuboid sample was processed to get a PEO pre-coating with thickness around 50 μm; after drying, various sealer materials were directly spray-coated onto its top. Heat-treatment was followed to cure sprayed coating layer when thermoset seal material is utilized.

In HT aging test, coated sample was soaked into 3% KCl solution, and heated in an autoclave at 150 °C under 0.5 MPa nitrogen pressure for two days. After aging, samples were rinsed with deionized water, and dried for further analysis. To examine the coating microstructure, coated sample was sectioned with a precision saw, embedded into epoxy with standard hot mounting press, and polished to a mirror surface. Microstructure of coatings, as well as their interfaces with base, was then characterized by Keyence VHX-700 digital optical microscope (OM).

III. RESULT AND DISCUSSION

A. Conventional Delay Coatings

Since the ultimate goal is working temperature at 150 °C and above, suitable coating should be either inorganic or polymers with high thermal stability in hydraulic conditions. For this, various HT rated and chemically inert polymers which are broadly used in oil and gas industry, including PTFE, PEEK, PPS, ECTFE, etc., have been examined for their performance in delaying DM dissolving. As reference, tests on these materials themselves have confirmed that they are thermally stable and

chemically inert in working environment (3% KCl solution and 150 °C) for days without any degradation. However, when coated on to DM parts, these polymer coating prepared by standard industrial spray coating technology all failed to protect/delay DM parts from dissolving even at low temperature (< 100 °C). We found that all these polymers have similar failure mode. Taking ECTFE coating as example (Fig. 1 (a)), the coating typical breaks at edges or corners, allowing corrosive fluid infiltrating into polymer/metal interface, and then got detached from metal base quickly with assistance of hydrogen gas pressure generated during DM dissolving process (i.e., reaction of Mg with water [9]). To improve bonding between coating and metal base, different primers have also been tried, however, they made little difference in final performance. OM characterization shows that polymer spray coating is typical thin at part edge (Fig. 1 (b)) and is also full of pin holes and other defects. Due to large difference in thermal expansion coefficient between Mg base ($2.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and ECTFE coating ($5.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), we believe thermal stress generated during HT aging process could easily crack inferior thin coating at edge/corner area and caused such failure. To improve coating thickness at corner area, overall coating thickness has been gradually increased up to 500 μm (the limit above which DM parts cannot assembled), and the aging tests showed same detachment failure mode. Improving coating thickness does not address this issue.

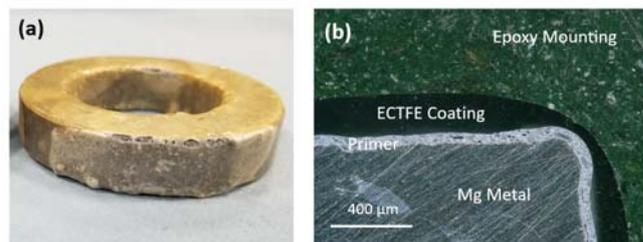


Fig. 1 Photo of failed polymer coating after aging (a) and OM image of ECTFE coating at sample edge area (b)

Besides polymer coatings, various popular inorganic coatings [13], including plating, chemical conversion & PEO, have also been tested at elevated temperature in hydraulic condition, which also failed at elevated temperature (not shown). Even though corrosion is most severe around edging area, coating detachment does not occur, which shows that inorganic coating bonds well onto base. However, these inorganic coatings are not “dense” enough to isolate Mg base from aggressive fluids, thus degrades more “uniformly” compared with polymer coating [14]. Among them, PEO coating shows the longest delaying time before failure, even moderate improvement over polymer coating, Microstructure analysis shows that PEO coating has more cracks and other defects at edge area (Fig. 2 (b)) and thus always fails first at edge area (Fig. 2 (b)). Most PEO coatings, especially in the outer region, are also porous (Fig. 2 (b)), which is consistent with reports that PEO typical has three layers: porous outer layer, intermediate dense layer, and thin inner dense layer,

respectively [15]. The latter two layers are most responsible for corrosion resistance, but not thick enough to delay severe corrosion in downhole conditions. Any mechanical damage during operation (common in oilfield) could lead to coating failure. Therefore, an effective sealer needs to be applied to block porous layers, making full usage of these tough thick layers. Commercial sealer material based on epoxy was tested in HT hydraulic environment, and seal layer detached from PEO coat very quickly. As water diffusion rate within epoxy is high, especially in HTHP condition, corrosive fluid could penetrate the sealer layer and corrode the PEO/Mg base. Therefore, advanced seal material needs to be developed to block porous PEO layer effectively at HT (> 150 °C) and corrosive environment.

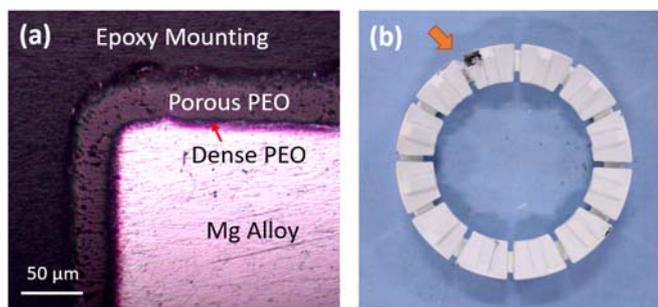


Fig. 2 OM image of PEO coating at sample edge area (a) and PEO-coated DM part after aging (b)

B. Coating plus CVD Sealing

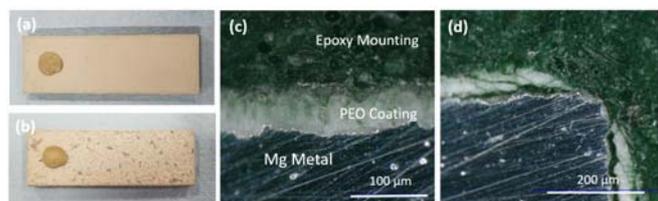


Fig. 3 Photo of CVD sealed PEO coating sample before (a) and after (b) 150°C aging test, OM image of such coating at flat (c) and edge area (d)

Since the material is deposited directly from gas state, Chemical Vapor Deposition (CVD) coating is supposed to be more effective to block open pores within porous PEO layers. In this study, SiO₂, thermal/chemical stable in working environment and compatible with PEO materials, is selected as sealer material, and directly deposited onto PEO-coated sample through industrial CVD coating process [16]. However, this sealer does not show obvious improvement. As shown in Fig. 3 (a) and (b), this coating breaks into pieces after 150 °C aging test. OM analysis shows that CVD coating is too thin to provide effective sealing (Fig. 3 (c)), as epoxy mount material (shown in green) easily infiltrates into porous PEO layer during hot molding process. In addition, the CVD coating process, typically high temperature > 400 °C, also causes thermal cracks and break PEO coating in the weak edge/corner area. As shown in Fig. 3 (d), PEO coating on edge is chipped away breaking surrounding coating into pieces, therefore allowing

green epoxy mount material to infiltrate between PEO/Mg base during sample preparation. Considering high cost and low effectiveness, CVD coating as sealer is proven to be not suitable for DM plug applications.

C. PEO Coating plus Fluoropolymer Sealing

Chemically and thermally stable fluoropolymer plus PEO coating has been reported to be successful in protecting flat DM surface in oil and gas [17], and effectiveness of this technology is also tested in this study on complex DM parts with edge/corners. After 150 °C 2 days aging, a fluoropolymer sealer material itself is found stable, however, the whole coating was detached from PEO base (Fig. 4 (a)). OM analysis shows that PEO coating is intact after seal spray coating, and the fluoropolymer sealer layer is effective into blocking porous PEO layer as green epoxy mounting material cannot infiltrate into PEO porous during sample preparation (Fig. 4 (b)). Sealer coating is uniform among flat area with thickness between 20-50 μm, but very thin at the edge/corner area. High resolution OM image at sealer/PEO interface area shows that the fluoropolymer does not infiltrate into PEO porous layer very deep, and voids between sealer and PEO coatings are broadly observed (Fig. 4 (c)). Since the chemical inert fluoropolymer has little affinity with PEO coating (thus low contact angle) and also high viscosity when melted during spray coating process, sealer material does not have enough driving force to deeply infiltrate into PEO pores, just forming a weakly bonded layer on its top. Therefore, it could be easily detached from PEO surface during thermal cycle as result of thermal stress from edge/corner area where polymer coating quality is poor, a failure mechanism broadly observed on polymer spray coating is discussed in Section A (Fig. 1).

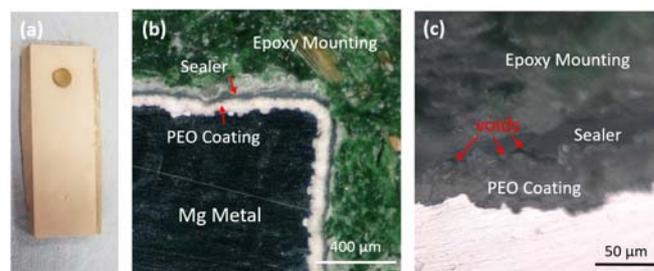


Fig. 4 Photo of a fluoropolymer sealed PEO coating sample after 150 °C aging test (a), OM image of this coating at edge area (b), high magnification OM image of coating microstructure (c)

To increase the sealing effect, especially at edge/corner area, we increased the seal thickness from 20 μm to almost 400 μm, as shown Fig. 5. It is true that coating thickness at the edge is still much lower than that in flat area, however, it is still over 50 μm thick, and fully protects all the base material under edges. According to high magnification OM analysis (Fig. 5 (b)), interface between sealer and PEO is the same, i.e., full of voids. After aging at 150 °C for 2 days, the whole coating fails in the same way as thin coating, starting from edge and finally detached from PEO base. Besides, other thickness in between (i.e., 100 μm and 400 μm) were tested, and the results are the

same. It indicates that modifying sealer thickness does not improve protection if the bonding between sealer and PEO base is weak. Thermal stress, caused by thermal expansion mismatch between seal ($5.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and PEO coating ($1.1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$) during HT aging process, could easily break the weak edge area regardless of its thickness ($< 500 \text{ } \mu\text{m}$ in concerned range), a phenomenon also observed in thin polymer spray coating without PEO under layer (Fig. 1).

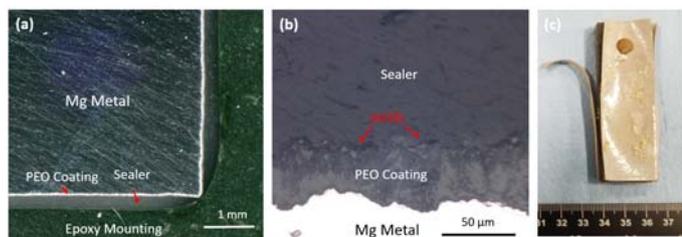


Fig. 5 OM image of thicker fluoropolymer sealed PEO coating near edge area (a), high magnification OM image of coating microstructure (b), and photo of coating sample after 150 °C aging test (c)

D. PEO Coating plus HT Thermoset Sealer

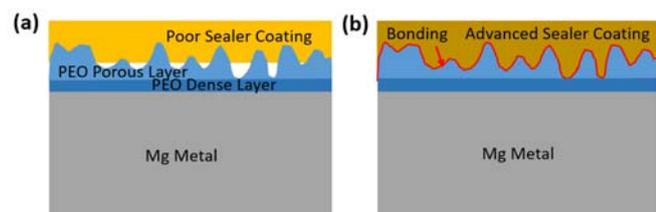


Fig. 6 Schematic illustration of poor seal (a) and high quality sealer (b) microstructure

Poor interface between PEO/fluoropolymer sealing layers is caused by low affinity of fluoropolymer to PEO layer, and its high viscosity in the molten state during coating process as result of its large molecular weight as thermoplastics, which both prevent fluoropolymer melt from infiltrating into porous PEO layers deeply (Fig. 6 (a)). To address this issue, sealer material, with both strong bonding to PEO and extremely low viscosity [18], needs to be developed to achieve a perfect design as illustrated in Fig. 6 (b). Therefore, a thermoset resin was finally selected with following properties: (1) dense and super hydrophobic to isolate fluid, (2) thermal/chemical stability in working condition, (3) higher affinity/bonding to PEO under-layer, and (4) most importantly reasonable elasticity or ductility to reduce thermal stress at edge during thermal cycling (Fig. 5). Besides, a volatile solvent is also added to such thermoset monomers to further reduce its viscosity, assisting infiltrating process during spray coating. A thin layer of such coating ($50 \text{ } \mu\text{m}$) was applied to PEO (Fig. 7 (a)) and OM analysis shows that these sealer materials penetrate deeply into porous PEO materials and no voids can be observed at sealer/PEO interface (Fig. 7 (b)), a structure similar to design illustrated in Fig. 6 (b). After aging at 150 °C for 2 days, no obvious change can be found for this coating. Of disclosed coating systems, it is the first thin coating in oil and gas industry that can delay DM complex parts (with sharp

corners) in corrosive fluid at 150 °C for over 2 days. As reference, thin coatings of this sealer material without PEO under-layer, regardless its thickness, have also been tested, and DM samples fails very quickly even at low temperature ($< 100 \text{ }^\circ\text{C}$, not shown). Therefore, the significant improvement of this PEO/sealer system can be attributed to a synergistic effect between porous hard PEO coating and chemical inert elastic-polymer sealing. With this microstructure design, aggressive fluid has been efficiently isolated from reaching to PEO dense layer under thermal cycles; the diffusion to the Mg base was significantly reduced.

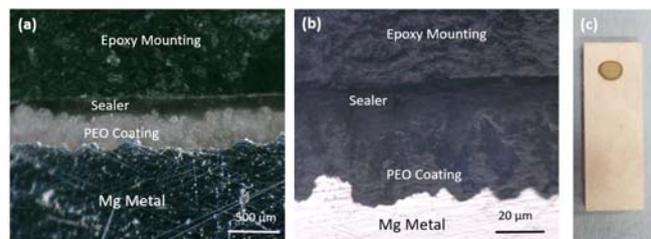


Fig. 7 OM image of thermoset sealed PEO coating (a), high magnification OM image of coating microstructure (b), and photo of coating sample after 150 °C aging test (c)

IV. CONCLUSION

In this study, we systematically examined failure mode of various common industrial coating technologies, and found that thermal mismatch between polymer coating and inorganic base, as well as poor coating quality in difficult areas (i.e., edges, corner, concaves), leads to failure in protection of DM parts with complex geometries in downhole conditions. To address this issue, we developed a PEO-elastic sealer system with synergistic effects between porous hard PEO coating and chemical inert elastic-polymer sealing. PEO under-layer, especially the dense inner layer, provides corrosion protection, while elastic HT sealer effectively plugs all the open pores of PEO outer porous layers under thermal cycles. To achieve this better sealing performance, sealer material needs to meet following requirements:

- 1) extreme low viscosity to infiltrate into porous PEO layer efficiently
- 2) high hydrophobicity to isolate downhole fluids,
- 3) high thermal/chemical stability in working condition,
- 4) high affinity/bonding to PEO under-layer
- 5) reasonable elasticity or ductility to reduce thermal stress at edge during thermal cycling.

Besides thermoset polymer used in this work, various polymer structures with functional groups can be designed and synthesized to better meet these requirements, which would be promising for even higher temperature application and worth extensive investigation in the future work.

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