

DISCUSSION ABOUT MAGNESIUM PHOSPHATING

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The paper describes results from recently published research focused on production of non-conventional magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ – bobierrite, or $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ – newberyite) coating for both magnesium alloys and/or mild steel. This new kind of coating is categorized in the context of current state of phosphating technology and its potential advantages and crystal structure is discussed. At the same time, the suitable comparison techniques for magnesium phosphate coating and conventional zinc phosphate coating are discussed.

Key words: mild steel, magnesium alloy, magnesium phosphating, bobierrite, newberyite

INTRODUCTION

Phosphating is a popular surface treatment for both steel and other metals (Zn, Al, Mg) and their alloys. Various porous coatings of nonsoluble phosphates enhance adherence of paints and prevent corrosion attack between the layers in the case of damage to the organic coating compromising its integrity [1, 2].

Conversion coating is formed on suitably prepared surface of metallic samples by joint influence of cations and anions – cations are formed by the corrosion reaction between the base metal and the phosphating bath; the anions come from the phosphating base itself. Depending on the dominant cation, the dihydrogen phosphate baths are often categorized in several groups: zinc, zinc - calcium, magnesium and multi - cation [2]. However, the standard EN ISO 9717 specifies the phosphate coatings by their mass per area and the application purpose [3]. Most common multi - cation phosphate coating is the “tri - cation” which found its place in the same industrial applications as the other above mentioned phosphate coatings.

The “tri - cation” phosphate bath is very similar to common zinc phosphating baths, however the concentration of Zn^{2+} is reduced and the Ni^{2+} , Mn^{2+} , Co^{2+} (and sometimes also Mg^{2+}) cations are added [1, 3, 4].

Such baths produce coatings comprising by majority of $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (phosphophyllite) instead of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, i.e. hopeite. Phosphophyllite is, due to the higher iron content, more resistant in alkaline environment and is therefore preferred over hopeite as surface treatment before E - coating. During this process, alkaline environment is formed in the diffusion layer of coated component [1, 4].

Addition of magnesium cations to the baths (as well as other cations: Ni^{2+} , Mn^{2+} , Co^{2+}) in the “tri - cation”

phosphating conclusively facilitates deposition of phosphate coating and with their contribution, more compact coating with higher corrosion resistance is formed [2, 5].

Phosphating baths for production of magnesium-dominant phosphates coatings have not yet been conceived. The reason is probably the water solubility of magnesium ions [5].

If the composition of a new bath capable of reliably forming magnesium phosphate on the surface of different metals is successfully defined, it could replace some of current phosphating technologies [6].

Magnesium phosphating of magnesium alloys

In 2009, the first paper about possible application of magnesium phosphate coating on magnesium alloy AZ31 was published [7]. The reason for specifying completely new phosphating bath is the effort to create completely unique coating with extraordinary corrosion resistance on magnesium alloys [7].

The discussed phosphate coating was not yet prepared by conventional phosphating technologies. After immersion to the work bath (mixture of diluted ortho - phosphoric acid (1:10) and solution of α - Ca_3PO_4 (8,5 $\text{g} \cdot \text{l}^{-1}$ / 300 ml) prepared by 1:1 mixing) the MgHPO_4 coating precursor was formed within one minute. This is described by the reaction (1):



The sample of AZ31 is then exposed for 72 hours at 50 °C in glass container filled with work bath.

This procedure forms highly rough coating, consisting of cubic, sheet up to paneled crystals of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. This compound is called newberyite and crystallizes in orthorhombic lattice.

Prepared crystalline coating has thickness up to 50 μm and provides the underlying metal with increased corrosion resistance and also enhances its wettability.

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Good adherence of the coating was verified by scratch test, i.e. measurement of scratch critical load; the average value was about 15 mN [7].

All the mentioned properties suggest that the new type of phosphate coating can be theoretically used even as an anti - corrosion surface treatment of bio implant bone replacements made from magnesium alloy.

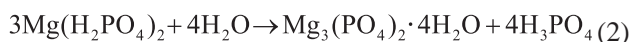
In this application, the porosity and brittleness must be taken into account. At the same time, their wettability, adherence, tissue biocompatibility and degree of surface coverage must also be verified in the case of application on rugged surface replacement (screws etc.) [6, 8].

Magnesium phosphating of mild steel

Phosphate coatings are often used as surface treatment for mild steel. It has been mentioned before that these coatings are most commonly used to enhance adherence and overall corrosion resistance. Recently (2013), uniform coating of magnesium phosphate (bobierrite) was successfully prepared.

bobierrite coatings

In the 2004, M.F. Morks successfully deposited uniform coating comprising of tertiary magnesium phosphate (bobierrite – $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) [9]. The coating on the mild steel was prepared by dipping into work bath (55 °C, 3-5 min). The bath was prepared by diluting MgCO_3 paste by diluted ortho - phosphoric and nitric acid. The author defines the parameters of the bath by points (also used in industrial practice): total acid - 17 points; free acid - 1 point. The bath was adjusted by accelerator (NaNO_2 - 0,5 g·l⁻¹) and salts: Ni^{2+} (2,5 g·l⁻¹), Mn^{2+} (1,2 g·l⁻¹) and Ca^{2+} (1,5 g·l⁻¹). Effect of pH (adjusted by NaOH) pH = 2,5; 2,78 and 3,0) on the quality of produced coating was also studied. The XRD data suggest that ideal conditions are pH = 3 and the immersion time is 5 min. Moreover, the author verified that the amount of produced dregs increases exponentially at pH > 3,0. Produced tri-phosphate coating is uniform; its mass per area is 3 g.m². Author described the formation reaction (2) as:



On the steel surface, the leaf - like shapes in petal arrangement are formed. The total length of these shapes is 10 - 15 μm.

In practice, the performance of produced coating is compared to the hopeite coating ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) formed by the conventional zinc phosphating (5 min, pH = 3). The comparison is done directly by neutral salt spray test (NSS).

Organic coating is deposited on the phosphate-coated samples and both coatings are scribed to the base metal marking "X" on its surface. The corrosion attack was evaluated visually after 150 hours of exposition. Based on this test, the bobierrite coating was given sim-

ilar corrosion resistance rating as the common zinc-phosphate coating (hopeite) [9].

Nevertheless, from the industrial application point of view, this comparison cannot be considered a definitive one. The zinc phosphating technology is capable of producing various coatings in terms of thickness, porosity, grain size and even composition. It is therefore necessary to continue in the compare studies – verify the porosity and corrosion resistance by electrochemical measurements. The thermal stability of bobierrite also needs to be verified.

The paper describes the structure of magnesium phosphate in detail; however detailed description of structure of zinc phosphate, to which it is compared, is missing.

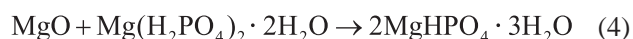
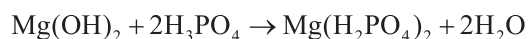
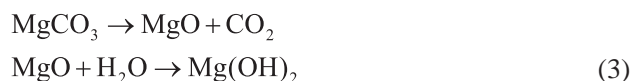
The crystallographic data suggest that the bobierrite crystallizes in orthorhombic lattice of the Cmc2₁ symmetry group. Grains of this mineral can bind variable number of water molecules and thus form 3 other hydrates, i.e. $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ or $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ or eventually $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$.

It is therefore not possible to rule out that these hydrates will not be present in the coating produced on steel [10].

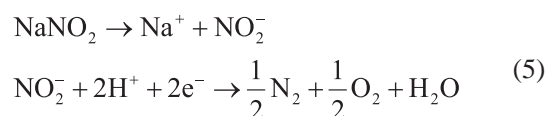
Newberyite coatings

In 2013, an article was published about preparation of uniform $\text{MgHPO}_4 \cdot 2\text{H}_2\text{O}$ layers (newberyite) on steel, similarly to layers on magnesium alloys [11, 12]. The procedure of depositing secondary magnesium phosphate (also called magnesium phosphate dibasic) on steel surface was described by M. Fouladi and A. Amadeh. The composition of working bath was specified by the authors as: 23 ml H_3PO_4 (85 wt. %); 8,5 g·l⁻¹ MgCO_3 ; 0,4 g·l⁻¹ NaNO_2 ; 6,8 g·l⁻¹ NaOH.

The procedure of coating is described by system of usual chemical formulae defining formation of typical soluble primary phosphate component ($\text{Mg}(\text{H}_2\text{PO}_4)_2$) (3) and subsequently the final formula of coating formation (4):



The authors reported acceleration of phosphate coating reaction using sodium nitrite according to conventional formulae (5) [12]:



The magnesium hydrogen phosphate coating has again sheet-like shape of petal arrangement; see Figure 1.

Authors are trying to optimize the conditions of quality coating of newberyite production, altering the

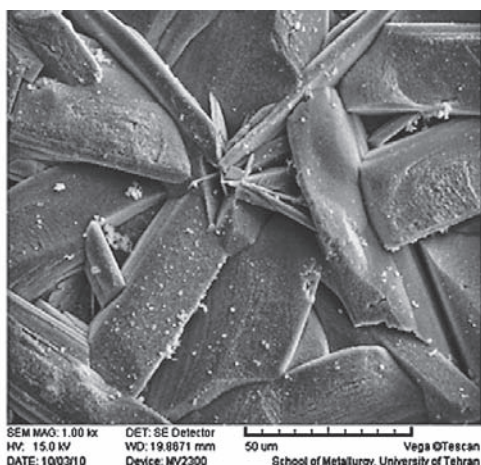


Figure 1 Morphology of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ crystals deposited on steel (reprinted from [12])

bath temperature (tested: 20 °C, 40 °C, 60 °C, 80 °C, 90 °C; exposure time 20 min) and exposure time (tested: 1 min, 3 min, 5 min, 10 min, 20 min, 30 min; at 80 °C). Surface quality is evaluated by the degree of surface coverage (SEM), electrochemical test to qualitatively measure barrier properties of the coating and its porosity. Other parameters, such as: time dependence of corrosion potential (E_{corr} /SCE), polarization resistance (R_p) and corrosion current density (i_{corr}) were also measured. Porosity was calculated from measured data. The amount of produced dregs was evaluated by gravimetric method [12].

The temperature of the work bath naturally affects the coating formation kinetics. Coating does not form at the temperatures of 25 °C and 40 °C. Coating at 60 °C produces unsuitable coating; however, bath of 80 °C evidently yields surface coverage of 100 %. The thickness of the phosphate coating (~ 30 μm) does not change for the samples coated in the bath of 80 or 90 °C. Conversely, coating in 90 °C bath produces twice the amount of dregs (amorphous). Data from electrochemical measurements suggest as well that the optimal temperature is indeed 80 °C – the coating formed at higher temperature has increased porosity. One theory suggests that at higher temperature, fewer phosphate seeds are formed and more porous coating is thusly formed [12].

If the new phosphating technology is to be implemented, optimal bathing time must be determined. Non-optimal phosphating cannot guarantee production of coating on 100 % surface, and also causes energy loss and coarsening of the coating. It is sometimes also suggested that growing phosphate grains can, by their expansion, push out other, less-adherent grains from the surface. Authors reported that in 10 minutes time, only non-uniform coating is formed. Uniform layer is formed after 20 minutes. After 30 minutes, the uniformity of coating again decreases – size of some grains increases dramatically. It has been demonstrated, that the amount of dregs increases significantly after ten minutes of exposure. The authors also shown that new

phosphate grains form on the surface of mild steel only during the first 5 minutes (nucleation stage). After this time, new grains stop forming and existing one grow in size. It was established by electrochemical tests that coating formed after 20 minutes is less porous than coating formed after 30 minute bathing [12].

Further, the overall corrosion resistance provided by the coating is compared to the common zinc phosphate coating ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) using the neutral salt spray test (NSS). Though this is not a common practice in industry as the phosphate coatings are not covered by organic coatings prior to the test. Authors noted that magnesium phosphate performs better in an environment of 3,5 % NaCl and 35 °C than the zinc phosphate coating [11].

However this can be only logical consequence of increased thickness of the coating (30 μm) contrary to the zinc phosphate (10 μm). From this viewpoint, the results are not comparable. It is necessary to determine their mass per area to obtain information about the coating compactness. Again, it is necessary to stress out that the technology of zinc phosphating can produce coatings of various thicknesses, mass per area weight and chemical composition. Comparative study used low-temperature phosphating bath (65 °C) without accelerator to produce the zinc phosphate coating.

CONCLUSION

The paper provides detailed sequence of magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) on mild steel and magnesium alloys. Due to complex application of phosphating in machinery industry as basic surface treatment before organic coating application, the research to enhance the quality of the crystalline surface itself must be further supported.

In recent years, the research has been focused more on improving the conventional technologies by addition of small amount of inorganic or organic compounds to produce more compact coating or reduction of amount of produced dregs etc.

Completely new kind of phosphate coating has not yet been discussed. Magnesium phosphating is potentially more suitable alternative to current coating technologies. However, the new baths should be able to produce coating of similar parameters (porosity, thickness, area weight, provided corrosion resistance in given environment etc.), without requiring operation at higher temperature or yielding high amounts of dregs.

Existing comparative tests cannot be considered completely relevant and finished. It will be necessary to compare corrosion resistance provided by the coating of similar area weight.

It is also important to verify the thermal stability of deposited magnesium phosphates, since easy dehydration of coating could render the coating unsuitable for some applications.

The obvious application of magnesium coatings would be the corrosion-resistant layer for bio implants

from magnesium alloys, however it also requires numerous number of tests before implementation.

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Note: The responsible translator for the English language is K. Štětková, CTU – Klokner Institute, Prague, Czech Republic