

Effect of Zinc Phosphating on Corrosion Control for Carbon Steel Sheets

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Abstract

For many years, phosphating is one of the recognized, Improvement of carbon steel for corrosion by using phosphating method, has been made. It can augment the design process and present a number of experimentally determined factors that should be applied to present work. This work approach to protection for bare carbon steel, different factor e.g., thickness, time of phosphating adhesion force, protection potential with phosphating and protection potential with phosphating and painting.

It is found that phosphating coating is proper to protect the carbon steel. The results conform to the theory of protection.

الخلاصة

لعدة سنوات خلت كانت عملية الأكساء بالفسفنة معروفة في تحسين خواص التآكل للفولاذ الكربوني. أن فحص قيم المتغيرات الخاصة بالفسفنة ثم تعزيزها وتطويرها خلال العمليات التجريبية والانتاجية من خلال تحديد العوامل المؤثرة في العملية. وفي بحثنا هذا تمت دراسة المتغيرات التالية (السمك ، زمن عملية الفسفنة، قوة الالتصاق، جهد الحماية مع الفسفنة، وجهد الحماية مع الفسفنة والصبغ). أن عملية الأكساء بالفسفنة كانت مناسبة وملئمة لحماية الفولاذ الكربوني بحيث ان النتائج أدناه كانت مطابقة لنظرية الحماية السطحية للمعدن.

Introduction

The use of phosphate coatings for protecting steel surfaces has been known since the turn of the century and during this period the greater part of the World's production of cars; refrigerators and furniture were treated this way. The first reliable record of phosphate coatings applied to prevent rusting of iron and steel is a British patent of 1869 granted to Ross. In the method used by him, red hot iron articles were plunged into

the phosphoric acid to prevent them from rusting. Since then numerous developments have taken

place, of which the major developments [2,3,4].

Phosphating is a conversion coating treatment largely used in many industries as a surface preparation for coating by paints and to increase corrosion resistance [1]. Phosphate layer on ferrous or non-ferrous metals [8–12] improve their surface properties by changes in the physico-chemical properties. The main applications of phosphating are for paints adhesion, to increase corrosion resistance, to oil impregnation and to promote electrical insulation [13,14].

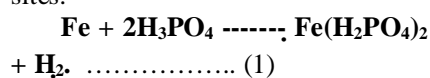
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Despite of their use for corrosion protection, phosphate layers by themselves do not produce considerable improvements in the metallic substrate corrosion using various additives, such as: nitrites, nitrates, chlorates, hydroxylamines, citric acids, calcium, nickel and manganese [15,16]. .

2- Chemistry of phosphating

All conventional phosphating solutions are dilute phosphoric acid based solutions of one or more alkali metal/heavy metal ions, which essentially contain free phosphoric acid and primary phosphates of the metal ions contained in the bath. When a steel panel is introduced into the phosphating solution a top chemical reaction takes place in which the iron dissolution is initiated at the micro anodes present on the substrate by the free phosphoric acid present in the bath. Hydrogen evolution occurs at the microcathodic sites.

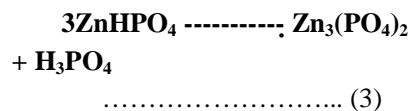
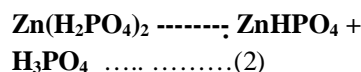


The formation of soluble primary ferrous phosphate leads to a concurrent local depletion of free acid concentration in the solution resulting in a rise in pH at the metal/solution interface. This change in pH alters the hydrolytic equilibrium which exists

between the soluble primary phosphates and the insoluble tertiary phosphates of the heavy metal ions present in the phosphating solution, resulting in the rapid conversion and deposition of insoluble heavy metal

resistance and need to be associated with other corrosion protection methods. Phosphating processes have been developed for many years,

tertiary phosphates. In a zinc phosphating bath these equilibria may be represented as:



A certain amount of free phosphoric acid must be present to repress the hydrolysis and to keep the bath stable for effective deposition of phosphate at the microcathodic sites [5,6].

3- Kinetics of the phosphating process

Studies on the kinetics of phosphating indicate that there are four distinct stages in coating formation Fig.(1) namely, the induction stage (a), the commencement of film growth (b), the main exponential growth stage (g) and the stage of linear increase in film growth (d). During the induction period, the oxide film remaining on the surface even after cleaning is removed. When film growth commences, the first nuclei are formed and the rate of nucleation increases rapidly with time. This, however, depends considerably on the conditions of the surface, the pretreatment procedures adopted and the oxidizing agents present in the phosphating bath. Growth occurs in the main exponential growth stage. Addition of accelerators reduces the

induction period and extends the stage of linear growth.

In the opinion of Gebhardt, the rate of phosphating depends on the rate of diffusion of Fe^{2+} ions from the structural lattice to the coating/solution interface through the coating formed. Machu has found that the rate of the phosphating reaction is a function of micro anodes on the surface.

$$-dF_A/dt = K \cdot F_A dt \dots\dots\dots(4)$$

where dt . change in time; F_A . surface area of anodes in micro cells; and K . reaction rate constant. The rate of formation of the phosphate coating depends primarily upon the metal viz., the ratio of anode surface which was initially present, F_A , to the anode surface at any given moment, F_A . The influence of various other factors controlling the rate of reaction, e.g., temperature, surface condition etc., is reflected in the value of the rate constant K , which is different for different processes [7].

4- Experimental Work

4-1 Research Directions

The main object was directed to coat with Zinc Phosphate at different operation conditions includes, time, thickness and surface preparation. The main properties which are studied like microstructures, adhesion force, protection potential with phosphating and painting.

4-2 Experimental Material

Experimental material which ,used are listed in Table 1.

4-3 Experimental Equipment

Experimental equipment which ,used are listed in Table 2 .

4-4- Working Specimen

Working specimens were of carbon steel with dimensions (6×6 cm).The metal specimens were placed in the phosphating bath at a depth of 10 cm below the solution and also 10 cm above the bottom of the solution in the stainless steel bath. The sheet specimen of carbon steel was analyzed by the specialized institution of engineering industrials. Baghdad. The results are summarized in table (3).

4-5 -Zinc Phosphate coating

As table (4) typical 9 stage Zinc phosphate process.

4-6 Bath Composition

The chemical composition of the concentrated zinc phosphating bath used in this study is shown in [Table 5](#).

6- Results and Discussion

6-2- zinc phosphating

The results are listed in Table 6 out lines a brief knowledge aspect of zinc phosphating technology especially on carbon steel sheets, depending on their surface preparation, time of immersion, thickness of zinc phosphate, adhesion force and protection potential.

6-2-Surface preparation

In this work four different solutions were prepared for cleaning and etching the specimens. It was found that the more effective solution, phosphating treatment process as follow, Degreasing , pickling , rinsing , phosphating , rinsing , chromic acid sealing and drying.

6-3 Phosphating Surface Characterization

The morphology of the phosphate layer was investigated by optical microscopy . The electrochemical behavior of the phosphate samples was analyzed by protection potential, thickness with time and adhesion . Figures (2,6) shows the phosphate grains are deposits as hexagonal plates and present a needle-like morphology. Chromates are the most efficient anticorrosion, which favor the passivation of carbon steel substrate at the sites of through defects of the phosphation [17]. As seen in the optical images Figures (2,6) , the size phosphate layer was formed on the carbon steel samples and the grain size of phosphate crystals strongly increased as the phosphation time increased until proper time (60 min) ,as in this work . It is shown in Fig. (2) that Zinc phosphate deposits on carbon steel sheet with different immersion time . A continuous Zinc phosphate layer covering the whole sheets surface with different thickness , the reduction in immersion time, means reduction in grain sizes aids the formation of a low uniform zinc phosphate coating with lower protection potential . It is shown from Fig(3) relation between immersion time and zinc phosphating thickness which is depended on many variables, such as concentration of

contents, temperature of bath and immersion time .

6-3 Effect of adhesion

Figure (4) show that the adhesion are improved by increasing thickness of zinc phosphate because of the film of zinc phosphate is to improve wetting, and then adhesion of the point film and corrosion protection of collective surface coating protection as fig (6).

6-4 Effect of structure

Fig.(2) shown phosphating treatments provide a coating of insoluble metal phosphate crystals that adhere strongly to the base metal and provide corrosion protection as Fig (5) and provide a base for adhesion of paints.

In Fig. (6) the interface of optical micrographs of zinc plated carbon steel specimens which are explore the effect of immersion time and thickness of zinc phosphating.

The above optical micrographs data highlight five points deserving some discussion:

1. The growth of a homogenous zinc phosphate this film on clean substance.
2. The effect of paint adhesion on clean substrate according to their preparation and thickness of thin film of zinc phosphate.
3. Conditions are reaches for good adhesion by providing smooth and spread surface as fig(4).
4. The zinc phosphate coating is non-conductive so it protects the specimen's surface from electrochemical oxidation that leads to rust and corrosion.

5. The matrix of the phosphate coating form capillaries that increase the surface area and provide a mechanical interlocking structures on which the paint can adhere which explore as Figures (2,6)).

7-Conclusions

- 1.Zinc Phosphate, coating weighty 10-25 g/m².
- 2.Zinc phosphate coating reaction is simply known as the reaction between phosphates becomes insoluble on the surface and form a layer with metal is color.
- 3.Application should be under control time, concentration, ph, and total acid are the parameters.
- 4.Passivation is used at the last stage of phosphating process, chrome including 0-1-10% concentration Passivation prevent air accumulation under paint cover.
- 5.Leaking chromic acid provides extra corrosion resistance because of Passivation neutralized the anions and caution that come with water.
6. Scratch based continuing corruptions are reduced.
- 7.Corrosion protection is increased by paint.
- 8.Fraction effect is reduced for continuous moving spare paints.

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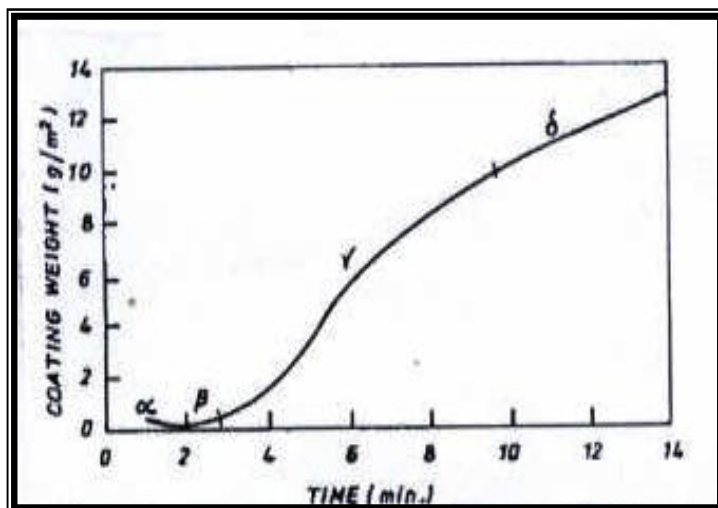


Fig (1) The various stages in the growth of phosphate coating (in presence of accelerator) [7]

Table(1) Material of Experimental Works

Coating Material	substrate	Electrolyte bath	inhibitors	Alkaline Cleaner	Pickling Solution	Solution volume
Zinc Phosphate	Carbon steel	Canphos e (101)	hexamine	NaOH, Na ₅ P ₃ O ₅ , Na ₅ CO ₃	HCl , Hexamine	10 liters

Table(2) Equipment of Experimental Works

Multi Rang Voltmeter	Reference Electrode	Power Supply
Floka,8000A,1000V	Saturated Calomel Electrode	Philips,10A,20V

Table (3) composition of carbon steel specimen

Element	C%	Si%	Mn%	S%	P%	Cr%
	0.1768	0.0052	0.3088	0.0211	0.0001	0.0001
	Mo%	Ni%	Cu%	V%	Fe%	
	0.0002	0.0001	0.0234	0.0025	Rem	

Table (4) typical 10 stage Zinc phosphate process

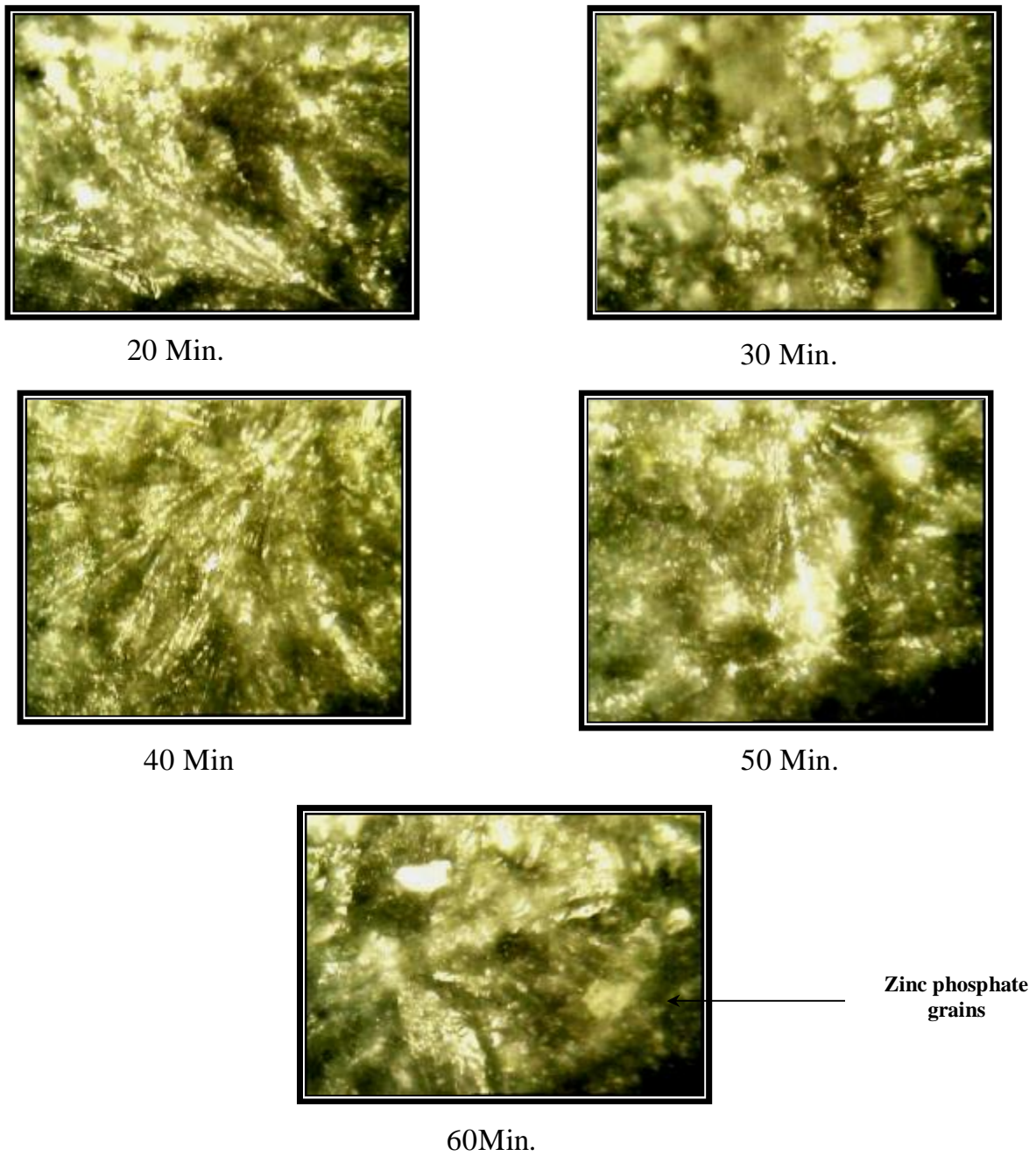
Material	D well time (min.)	Temp. °C
Alkaline clean	10	60
Water rinse	2	25
Pickling	10	25
Water rinse	2	25
Zinc Phosphate	20,30,40,50,60	95
Water rinse	2	60
Chrome steel	1	25
Water rinse	2	25
Dry off	5	120

Table (5) Chemical Composition of the Concentrated phosphating bath used.

Composition of Zinc phosphating Bath	WT. %
H ₃ PO ₄	28
HNO ₃	25
ZnO	19
NiCO ₃	0.8
H ₂ O ₂	0.2
H ₂ O	27.0

Table (6) Relationship between Time (min),thickness (μm), adhesion force (Kgf/cm²) and protection potential (mv)

Time, in (Min)	Thickness, (μm)	Adhesion force,(Kgf/cm ²)	Protection potential with phosphating only with [SCE(v)]	Protection potential with phosphating and painting only with [SCE(v)]
20	2	8	0.450	0.2
30	4	14	0.400	0.2
40	6	16	0.380	0.2
50	8	18	0.350	0.2
60	14	24	0.350	0.2



Fig(2) Optical micrograph of zinc plated phosphated carbon steel surface specimens for different immersion times (50X).

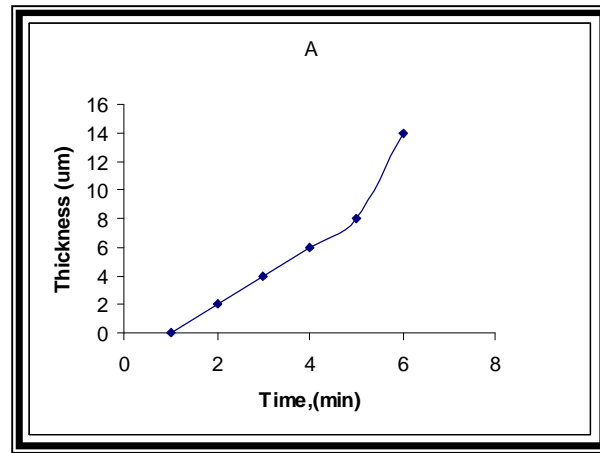


Fig (3) show the relationship between immersion time and the adhesion for five specimen.

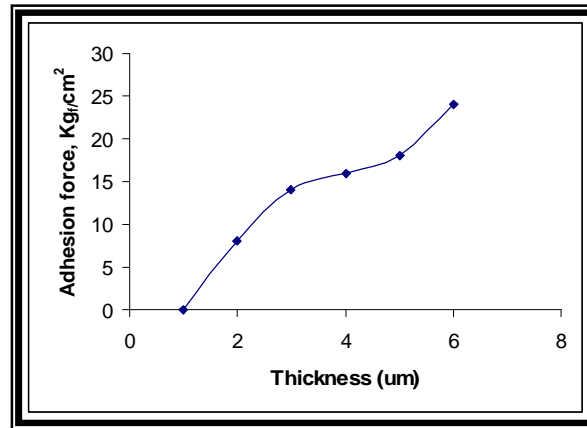


Fig (4) show the relationship between immersion time and the adhesion for five specimens.

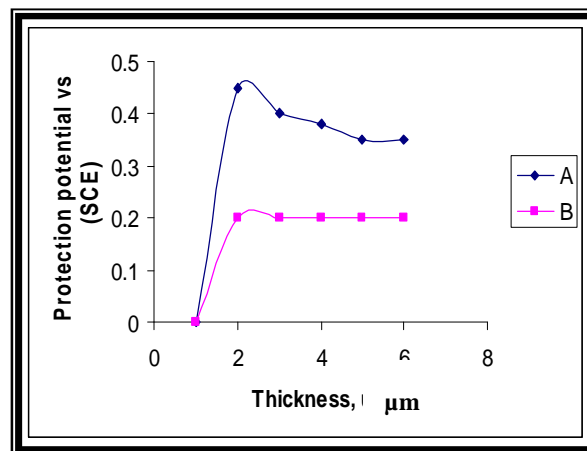


Fig (5) shows the relation between thickness and protection potential with phosphating and painting.

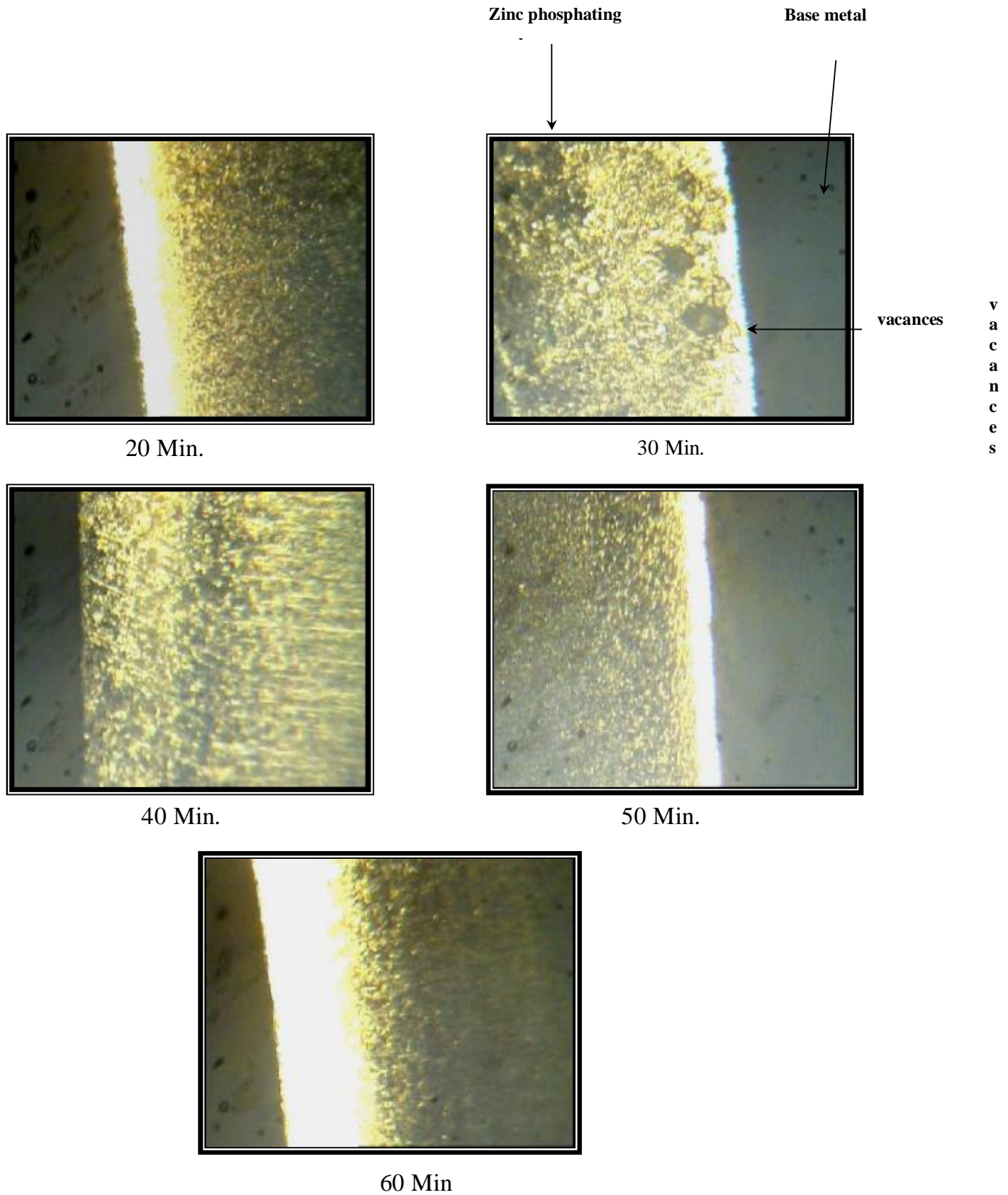


Fig (6) Optical microscope micrographs of zinc phosphating in interface specimens for different immersion time (50X).