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The Effect of Phosphate Coatings on Fatigue Crack Initiation in Quenched and Tempered Low Alloy Steel

R.A. Farrara* and J.C. Ritter

Abstract

Fatigue testing was performed on small notched bend specimens of AISI 4335 high strength steel used for cannon barrels, breech rings and blocks. The effect of surface coatings of zinc and manganese phosphate on fatigue life to crack initiation was determined at two levels of applied stress, selected to cause failures in the range of 1000 to 10 000 cycles appropriate to cannon breech mechanisms. Both types of coating drastically decreased life to crack initiation compared with uncoated samples, the degradation being attributed to surface pitting and crevice attack by the phosphating process.

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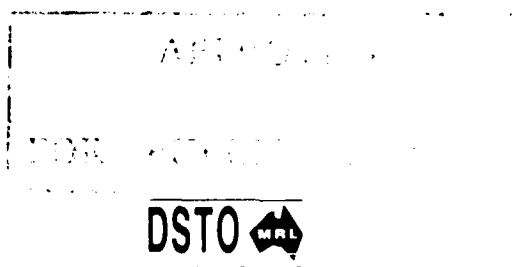
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MATERIALS RESEARCH LABORATORY

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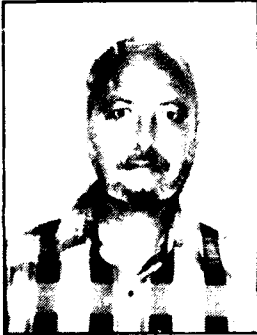
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The Effect of Phosphate Coatings on Fatigue Crack Initiation in Quenched and Tempered Low Alloy Steel

1. Introduction

The critical steel components of field guns (cannons) and howitzers - the cannon barrels, breech rings and breech blocks - are subjected to high levels of cyclic stress in service and are often life-limited by fatigue cracking. These components are generally produced from low alloy Cr-Mo-V steel that is quenched and tempered to give a material with both high yield strength, typically 900-1200 MPa, and high toughness, typically at least 2C Joule Charpy V-notch impact toughness at -40°C.

Protection of such critical components against corrosion is always a concern, especially in view of the extremes of environment where cannon may be operated. An accepted and widely used method for protecting these components is to apply a coating of either heavy manganese phosphate or zinc phosphate which is then given a supplementary coating such as oil or solid film lubricant. The manganese phosphate is typically used for both large calibre gun (cannon) components and other assemblies that have tightly toleranced moving parts because it is a soft crystal that mechanically retains an oil film which allows the coating to be "worn-in" smooth, and a low friction sliding motion is facilitated. Zinc phosphate is popular for non-moving parts because it is easily applied (immersion and/or spray processes) and has excellent corrosion resistance.

Both of these phosphating processes contain acids which attack the steel by etching. The etch pits, it was thought, may cause stress concentrations on the surface and thereby reduce the resistance of the steel component to fatigue cracking.

The objective of the present work was to determine what effect coating the surface with phosphate (zinc or manganese) has on the initiation of fatigue cracks in a representative high strength cannon steel. This report descrives a program of fatigue testing on small laboratory specimens, and the examination of their surfaces as-coated and after stripping to reveal the underlying etching attack.

2. Experimental

2.1 Specimens

Standard Charpy sized specimens 10 mm square × 55 mm long, with a 5 mm radius notch replacing the usual V-notch as shown in Figure 1 were used for the fatigue testing. Precautions were taken during specimen preparation in order to minimize the risk of overriding or masking the potential effects of the phosphating processes. These precautions were first, the use of a 5 mm radius notch which provides a known but small stress concentration factor (k_t = 1.25) [1] to control the location of cracking and second, the control of surface roughness on the radius to 2.5 μm maximum average peak-to-trough. This surface roughness in fact is representative of the typical roughness specified for gun components such as breech rings and blocks, hence the degradation in the resistance to crack initiation that resulted from the phosphate coatings can be viewed as representative of that occurring on actual components.
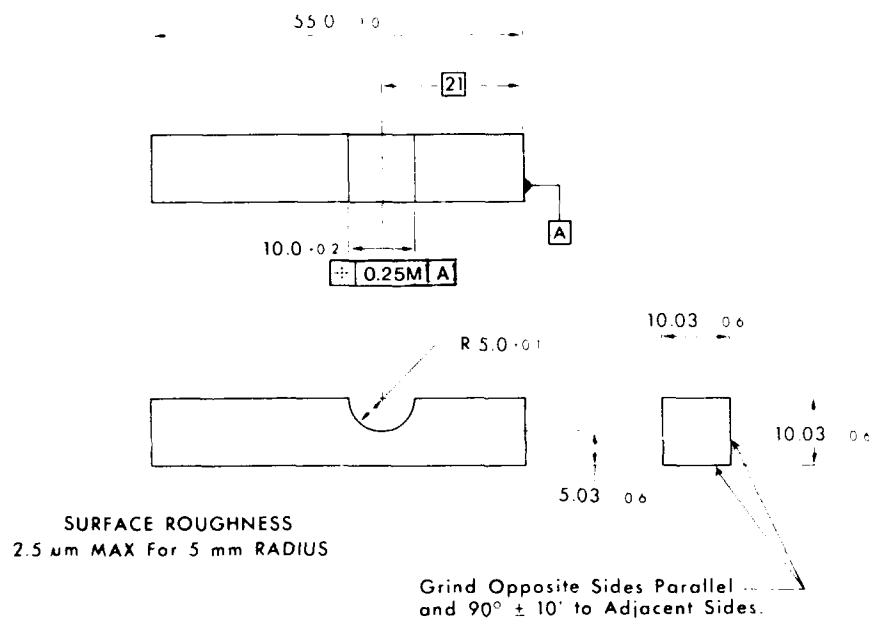

Figure 1: Test Specimen Geometry.

2.2 Material

Longitudinal specimens were removed near the mid-radius of a thick walled (240 mm OD × 90 mm ID) cylinder machined from the breech end of a 105 mm L119 gun barrel. This 1000 MPa yield strength steel was of the AISI 4335 vanadium

modified type, processed by electric furnace melting, vacuum degassing, and ladle refining by calcium treatment. A martensitic microstructure was produced by austenitizing at 880°C, water quenching, and tempering at 605°C. The composition and mechanical properties obtained from transverse specimens removed from the breech end of the gun barrel are given in Tables 1 and 2 respectively.

Table 1: Chemical Analysis of Gun Steel

Element	Code J100*	Actual
C	0.27/0.40	0.32/0.35
Mn	0.20/0.70	0.48/0.49
Si	0.10/0.35	0.24/0.25
S	0.012 max	0.007/0.010
P	0.012 max	0.011/0.012
Ni	3.00/3.60	3.44/3.49
Cr	0.70/1.20	0.98/1.01
Mo	0.50/0.80	0.69/0.70
V	0.10/0.30	0.26/0.26

Table 2: Mechanical Properties

Property	Code J100*	Actual
Yield Strength at 0.2% offset (MPa)	990/1110	1033/1045
Tensile strength (MPa)	-	1113/1125
Elongation (%) (GL = 5.65 √area)	9 min	11/12
Reduction in area (%)	25 min	34/37
Charpy V-notch Impact Energy at -40°C (Joules)	26 min	30/33.8

* UK Specification DEF STAN 10-13 Issue 2.

2.3 Phosphate Coatings

Two kinds of phosphate coating were applied, manganese phosphate by the Parker GM process, and zinc phosphate by the Turco Turcoat 4446 process [4].

The phosphated specimens were given the normal procedure of immersion in a chromate sealing solution that operates at a pH of 3.5-4.0, total/free acid ratio of not

more than 7/1, and at a temperature of 75°C. Removal of the phosphate from specimens after fatigue testing was accomplished by immersion in 5% chromic acid at 75°C for at least 10 minutes. Completion of removal was determined by X-ray analysis of the surface in the scanning electron microscope and monitoring the Zn and P peaks (Mn being effectively masked by Fe).

Details of the two phosphating processes are given in Table 3.

Table 3: Details of Phosphating Processes

Detail	Manganese Phosphate (Parker GM)	Zinc Phosphate (Turco Turcoat 4446)
Total Acid (points)	48 - 52	17 - 23
Free Acid (points)	Not less than 8	1.4 - 3.7
Total/Free Acid Ratio	Not less than 6	7 - 12
Bath Temp (°C)	85 - 90	80 - 85
Time in Bath (min)	20	30
Coating Weight (g/m^2)	9 - 11	15 - 16

2.4 Fatigue Test Equipment

The specimens were subjected to constant amplitude fatigue testing, using completely reversed (R = -1) bending moments at 25 Hz in a cantilever fatigue machine designed by the National Physical Laboratory in Teddington, England. The bending moment is determined by the amount of eccentrically located mass attached to a wheel that is belt driven by a synchronous motor rotating at 25 Hz (1500 rpm). Sinusoidal motion of the wheel is transmitted to the free end of the cantilevered specimen through vertical links attached to the spindle and a horizontal arm that contains one end of the specimen. The other end of the specimen is clamped rigidly. A schematic diagram of this specimen loading arrangement is shown in Figure 2 and the equations for calculating the bending stress are given in Appendix 1.

The machine is instrumented with strain gauges (full bridge configuration) attached to two of the canvilever bars [2]. The strain gauge bridge is energized by a regulated 6 V DC power supply, and the sinusoidal movement of the cantilever bars creates an AC voltage output that is amplified (gain of 100) and displayed on a millivoltmeter calibrated in RMS voltage levels. The peak voltage signal is monitored continuously and is used as a trigger to shut down the machine when the output peak reaches a pre-set level, usually set at 50 mV above the value displayed for an uncracked specimen. This shut-down device provides a simple and moderately reproducible control of final crack depth, usually of the order of 0.1-0.0.2 mm crack growth. Thus the criterion for failure requires that, after a crack is initiated, crack growth occurs rapidly so that the total number of cycles to failure is approximately the same as the number of cycles to initiate the crack.
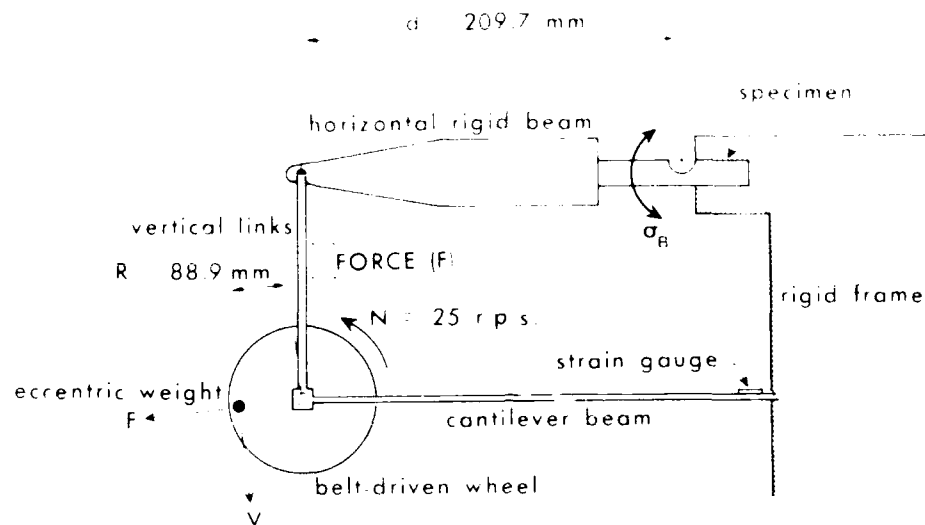
Figure 2: Schematic Diagram of Testing Machine.

2.5 Test Conditions

Four specimens with each of three surface conditions - uncoated, manganese phosphated, and zinc phosphated - were fatigued at each of two stress levels, making twenty-four specimens in all. Two stress levels were used to determine if the potential effect of phosphate coatings was a function of the applied stress.

The range of stress level was selected by trial and error testing of uncoated specimens, to have failures occur in the range of cycles appropriate to cannon breech mechanisms found in US Army experience, namely 1000 to 100 000 cycles. The stress level required to produce failure in an uncoated specimen in approximately 100 000 cycles was found to be 828 MPa (i.e. cycling at ± 414 MPa). The second stress level was arbitrarily set 50% higher at 1242 MPa (i.e. ± 621 MPa). In addition, a third stress level of 690 MPa (i.e. ± 345 MPa), which corresponds to the endurance limit for this steel, was applied to uncoated specimens.

3. Results and Discussion

The numbers of cycles for failure (N) at the various stress levels used for the three surface conditions are listed in Table 4. It is clear from these data that phosphating can drastically decrease the crack initiation portion of fatigue life. Using the mean values of life ($\bar{N}$) as the measure of difference between groups, the following statements can be made:

(a)   the deleterious effect of both phosphate coatings is equivalent within experimental limits;

(b)   the reduction in life ($\bar{N}$ uncoated / $\bar{N}$ phosphate coated) is significant and becomes greater as the applied stress is reduced - decreasing from a factor of approximately 3 at the low stress to a factor of approximately 1.5 at the high stress.

Table 4:   *Fatigue Test Results*

| Maximum Stress Amplitude (MPa) | No. of cycles to failure (N) | | |
	Uncoated	Mn Phosphate Coated	Zn Phosphate Coated
828	121 900	32 600	29 900
(± 414)	128 700	35 300	27 450
	107 700	39 100	30 850
	96 800	30 500	30 400
	$\bar{N}$ = 113 775	$\bar{N}$ = 34 375	$\bar{N}$ = 29 625
1242	6 100	4 500	4 300
(± 621)	7 800	4 200	4 100
	6 200	4 100	4 100
	6 675	4 200	5 300
	$\bar{N}$ = 6 675	$\bar{N}$ = 4 250	$\bar{N}$ = 4 450
690	817 000		
(± 345)	434 900		
	1 000 000, no failure		
	1 000 000, no failure		

Each tabulated value is the result of an individual fatigue test.

$\bar{N}$ is the average value of the four specimens.

The data are plotted in Figure 3 as the $\log_{10}$ of applied tensile stress (σ_B) versus $\log_{10}N$. Best fit straight lines, using a least square method through the data points, provide the following linear equations:

$$\log \sigma_B = m \log N + \log b \tag{1a}$$

that is

$$N = (\sigma_B/b)^{1/m} \tag{1b}$$

For uncoated specimens,

$$N_{uc} = (2.76 \times 10^{-4}\,\sigma_B)^{-8.09} \tag{2}$$

For phosphate coated specimens,

$$N_{pc} = (1.49 \times 10^{-4}\,\sigma_B)^{-4.96} \tag{3}$$

At values of stress above the cross-over point of the curves in Figure 3 (1360 MPa and 2745 cycles) the phosphate coatings have no effect on fatigue life. However, this level of stress is considerably above the yield strength of the steel and significant plastic straining of the surface region would be expected during cyclic loading.
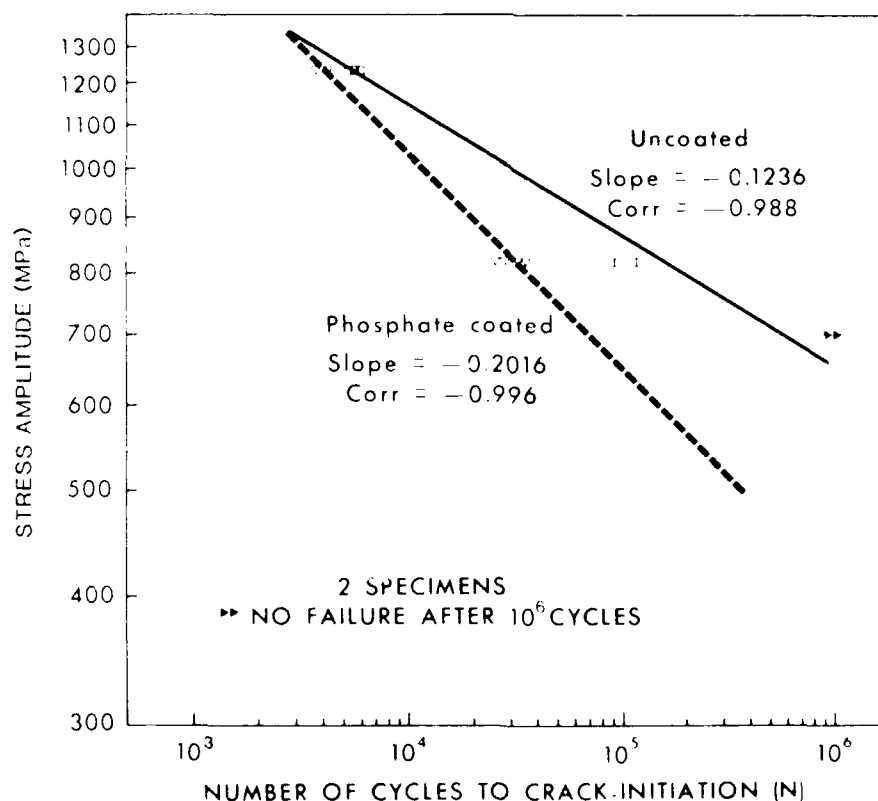

Figure 3: Fatigue Test Results - Phosphate Coated v Uncoated. Open square symbols refer to uncoated test specimens, open triangles refer to phosphate coated. R = -1 in all tests.

The increasing effect of the phosphating as the cyclic stress is reduced provides an insight into the basic cause of the deleterious effect on crack initiation. Figure 3 shows that small changes in the stress level result in large changes in fatigue life if the stress level is low, i.e. near the endurance limit, but small changes in stress result in small changes in life if the stress level is high, i.e. significantly above the endurance limit. A similar case is available in the literature, on notch effects [3], where comparison of the fatigue lives for notched and unnotched specimens of mild steel reveals a similarly large difference in life for the two specimens at a low nominal stress level, diminishing to a negligible difference in life at very high stress level (approaching UTS). This was attributed to the effective notch factor being close to the elastic stress concentration factor at low stress (and long cyclic life). As the nominal stress increased, the effective notch factor shifted closer to unity, reaching unity at the UTS when the life was one quarter cycle. That is, the notched fatigue strength approached the unnotched.
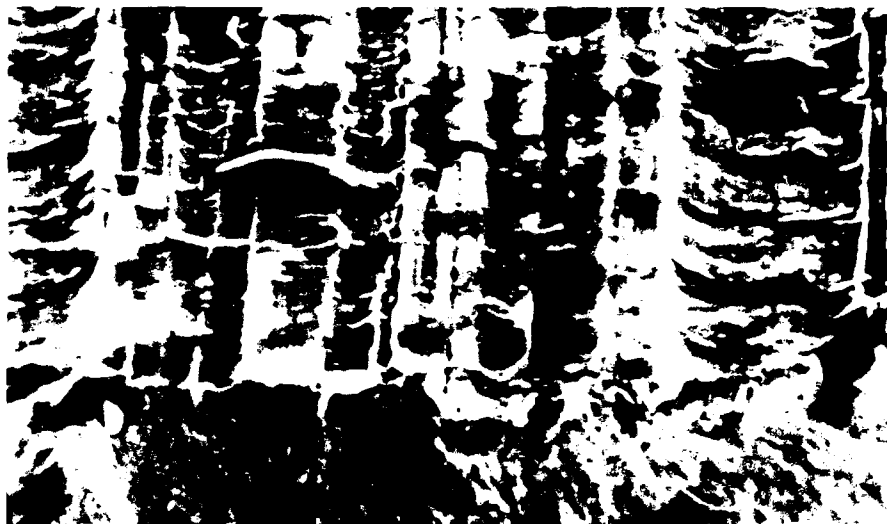
In terms of fracture mechanics concepts, a sufficiently high level of applied stress will lead to a large zone of localized plasticity at the tip of a small notch (in the case of a large etching pit), sufficient to extend beyond the depth of zone containing damage from the phosphating process. Thus the effect of phosphating is effectively masked, and there will be no difference between the fatigue performance of coated and uncoated specimens; the applied stress will be above the cross-over point of 1360 MPa in Figure 3. As the applied stress is lowered, the mechanical plastic zone diminishes with respect to the phosphating notch pits, thereby "unmasking" the phosphating damage and so leading to uncoated specimens exhibiting increasingly longer fatigue lives than the coated ones.

Examination of the specimens tested was made by optical metallography and scanning electron microscopy (SEM). Figure 4A shows the relatively shallow grooving on the as-reamed surface of the 5 m radius notch left uncoated, while Figure 4B shows the fatigue crack initiation from this surface.

A. Metallographic section showing surface roughness of the reamed grooves.
Unetched X400

Figure 4: Details of cracking from the as-reamed, uncoated surface.

B. *Fatigue crack initiation from the as-reamed surface. Reaming grooves in upper part of field of view, fatigue crack surface is in lower part. SEM X500*

Figure 4: *Details of cracking from the as-reamed, uncoated surface.*

Figure 5A shows the blocky crystalline morphology of the manganese phosphate coating, while Figure 5B shows fatigue crack initiation below this coating. Figure 6A shows the stripped surface, while Figure 6B gives a metallographic section revealing deep pits and crevices compared with the as-reamed surface (Fig. 4A). Figure 7A shows the distinctive platelet morphology of the zinc phosphate coating, while Figure 7B shows fatigue crack initiation. Figure 8A shows the stripped surface, and Figure 8B is a metallographic section showing surface pitting not so severe as beneath the manganese phosphate, and only partially obscuring the machining grooves.

While the surfaces beneath the phosphate coatings are significantly rougher than the as-reamed, because of pitting attack from the phosphating processes, it is possible that this geometric notch effect on the surface may not account for all of the marked reduction in fatigue life of the coated specimens. Recent work on fatigue crack growth in micro-notched specimens in similar steel has shown crack growth from surface defects as small as decoherent inclusions in the steel [5]. The deepest of the pits seen in Figure 6B is $\sim$ 20 μm, at which the 828 MPa cyclic stress will cause a stress intensity range of $\sim$ 7 MPa m$^{1/2}$ and corresponding fatigue crack growth rate of $\sim$ 5 $\times$ 10^{-6} mm/cycle (given by Figure 6 of Ref. 5). Therefore, on this basis the 0.1 - 0.2 mm crack growth necessary for the NPL machine used in the present work to switch off will require in the order of 2 $\times$ 10^4 - 4 $\times$ 10^4 cycles. However, the phosphated samples experienced a total life of this order, indicating a shorter time to crack initiation and possibly faster crack growth; this suggests an additional factor exacerbating the fatigue life.
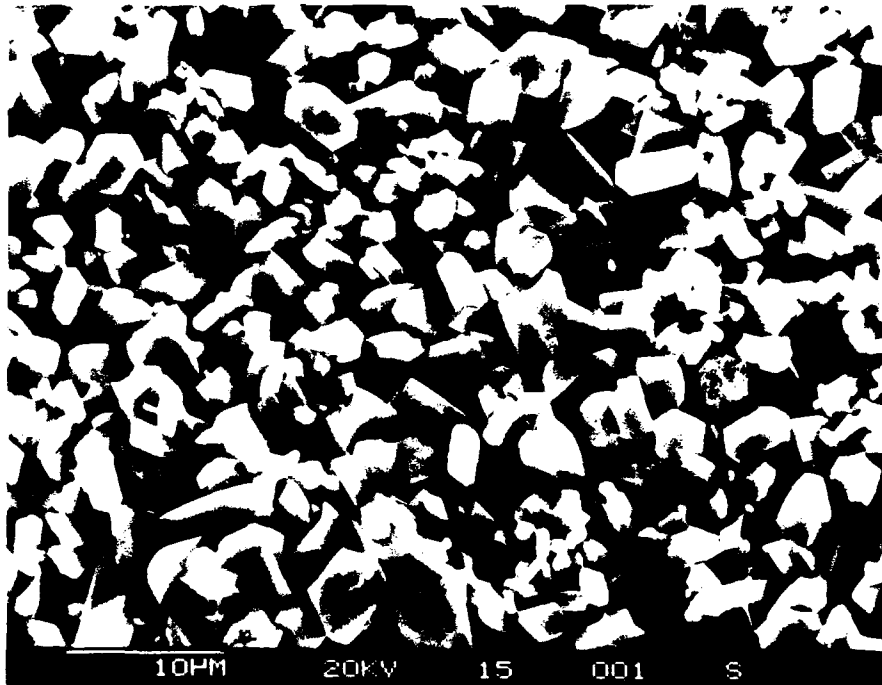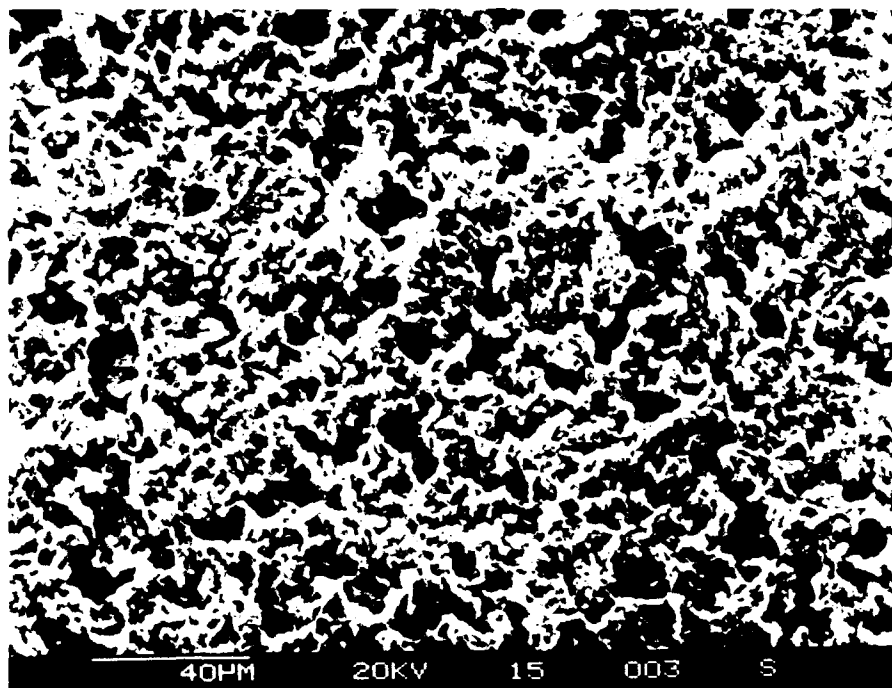
A. *Detail of coating morphology.* SEM X2000
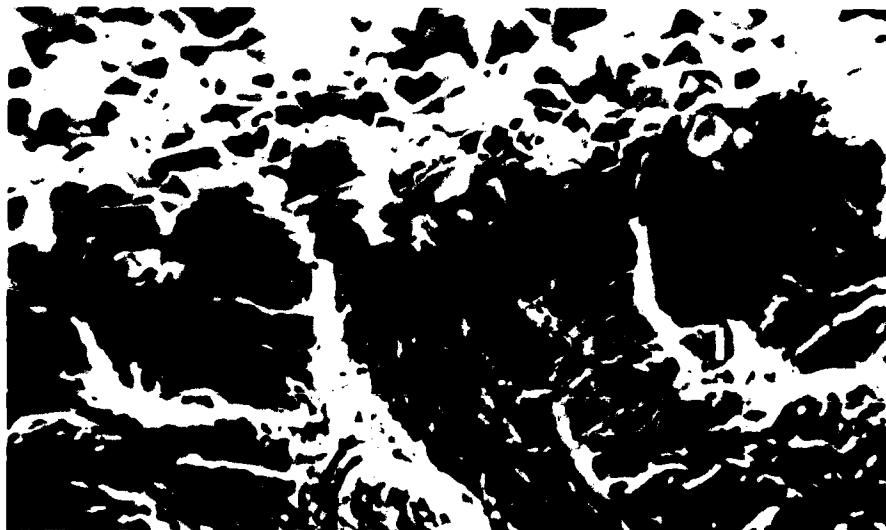
B. *Fatigue crack initiation beneath the coating.* Coating is in upper half of field of view,
fatigue crack surface is in lower half. Intergranular facets are indicated by I. SEM X500

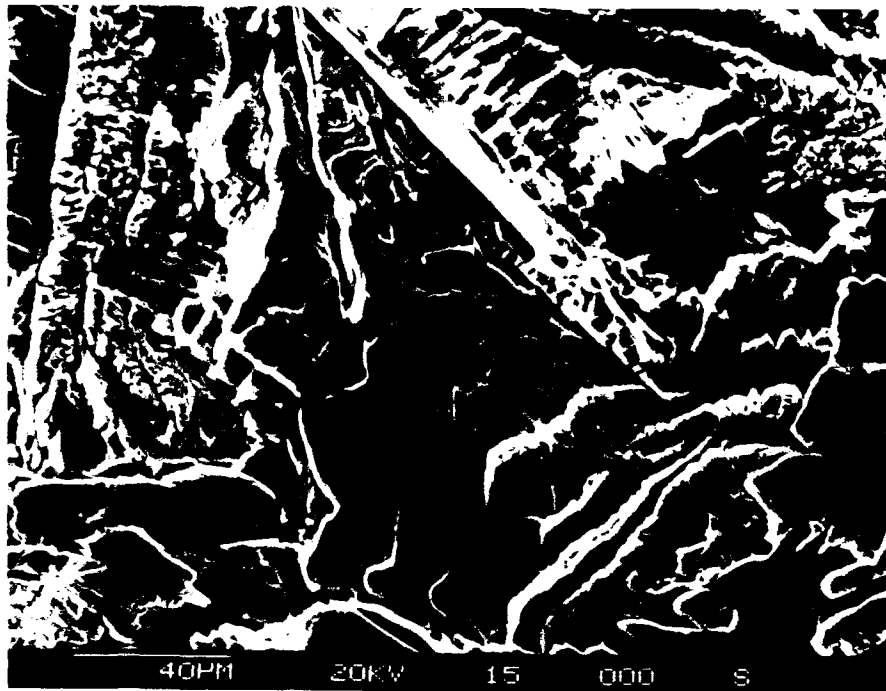**Figure 5:** *Fatigue cracking beneath the manganese phosphate coating.*
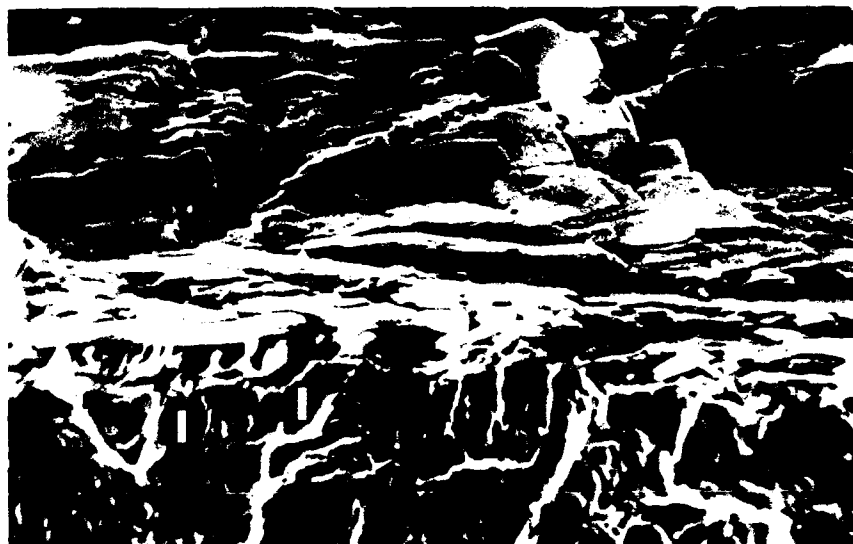
A. Stripped surface. SEM X500

B. Metallographic section showing surface pitting beneath the coating. Unetched X500

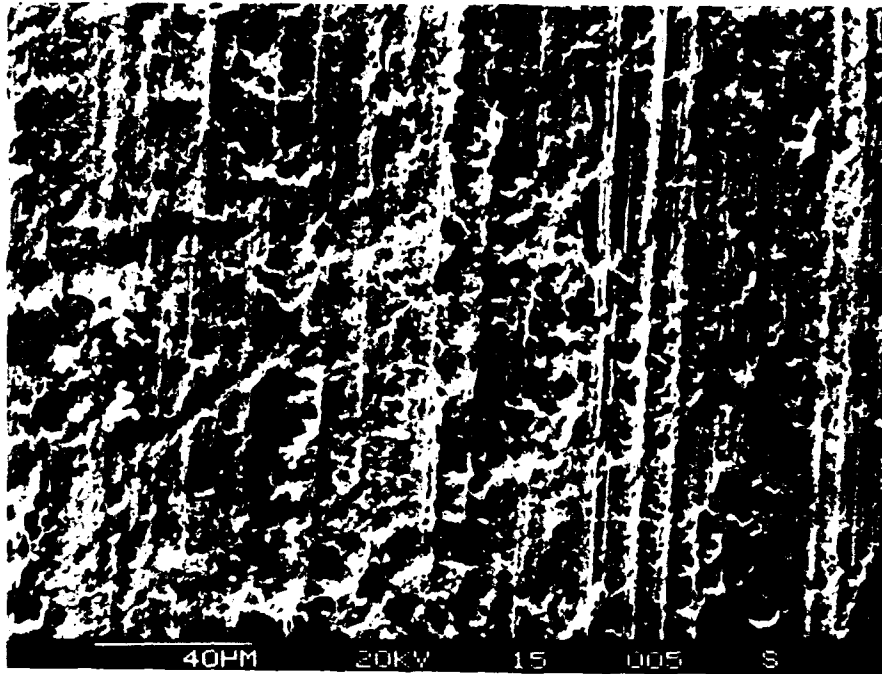**Figure 6:** *Details of surface beneath manganese phosphate coating.*

A. Detail of coating morphology. SEM X500

B. Fatigue crack initiation beneath the coating.   Coating is in upper two-thirds of field of view, fatigue crack surface is in lower third.   Intergranular facets are indicated by I. SEM X500

Figure 7:   *Fatigue cracking beneath the zinc phosphate coating.*

A. *Stripped surface. SEM X500*

B. *Metallographic section showing surface pitting beneath the coating. Unetched X500*

Figure 8: *Details of surface beneath zinc phosphate coating.*

A factor which must be considered here is the possibility of hydrogen charging under the acid conditions of the phosphating processes (Table 3). Hydrogen outgassing treatments are not normally required on such high strength cannon components and it has been demonstrated that hydrogen embrittlement significantly reduces the static notch tensile strength in these steels only when heat treated to above 1170 MPa yield strength [6]. There is some evidence that fatigue susceptibility is influenced by hydrogen at lower levels of yield strength, such that the present steel (1033-1045 MPa) falls within this regime [7]. The scanning electron micrographs (Figs. 5B, 7B) reveal fracture morphologies very similar to others' observations of fatigue cracking near the initiation regime [7]. The predominant fracture mechanism is a ductile transgranular one in which the influence of the underlying martensitic microstructure is apparent. There is a small number of steps and ledges which resemble fragments of brittle intergranular fracturing of prior austenite grain boundaries, and these are accepted as being caused by hydrogen diffusion to such boundaries. In the present case their small population and somewhat indistinct nature is consistent with this heat treatment condition being near the threshold of sensitivity to hydrogen [7].

On this evidence of hydrogen influencing - and accelerating - the early stage of fatigue crack growth, it is highly likely that the overall process of initiation and growth has been accelerated in the phosphated samples.

4. Conclusions

1. A manganese or zinc phosphate coating on high strength, quenched and tempered, low alloy steel has reduced the number of fatigue cycles required to initiate a crack at low applied stress. The degradation in fatigue life was the same for both types of phosphate coating.
2. The magnitude of reduction in fatigue life for a component coated with phosphate compared with uncoated depends upon the applied cyclic stress level - the higher the stress the less the effect from the phosphate.
3. It is likely that the degradation in fatigue life results in part from the local stress concentrations - pits and crevices - created on the surface by the phosphating process, and in part from the synergistic effect of damage arising from hydrogen charging during the phosphating process.
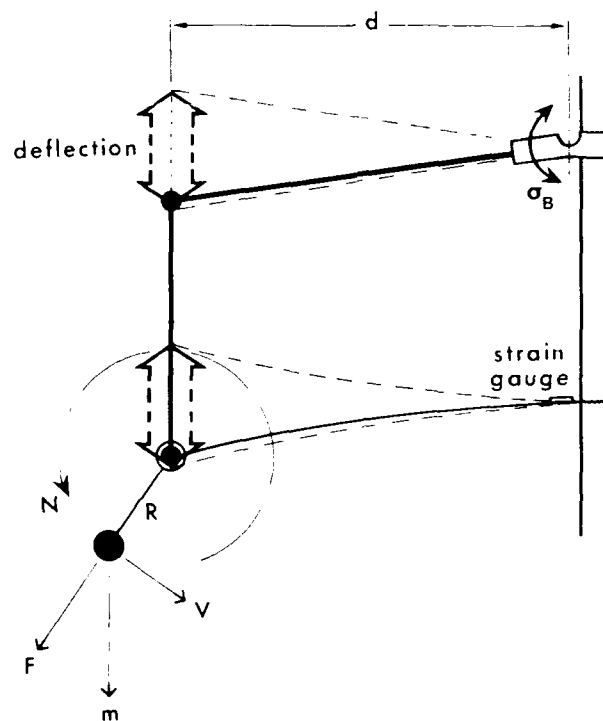

5. Acknowledgement

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Appendix 1

Equations for Maximum Bending Stress in a Cantilever Beam

$\sigma_B = \pm k\, MC/I\ (N/mm^2)$

$M = F \times d\ (N\,mm)$

$F = m\, V^2/R \times 10^{-6}\ (N)$

$V = 2\pi RN\ (mm/sec)$

$\sigma_B = \pm 13.80\, m\ (MPa)$

σ_B = max bending stress at 5 mm radius

k = stress concentration factor = 1.25 [1]

M = bending moment

$I/C = 10 \times 5^2/6 = 41.66\ (mm)^3$

m = mass in g
N = 25 Hz
d = 209.7 mm
R = 88.9 mm

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