

Influence of anions on the corrosion of high speed steel

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Corrosion potential measurements, voltammetric techniques and electrochemical impedance have been used to evaluate the corrosion resistance of M2 high speed steel in aqueous solutions containing chloride, bromide, iodide, nitrate, sulfate and perchlorate salts of sodium and potassium of varying concentration. The influence of changing the cation was found to be small and an order of anion aggressivity was established as: sulfate > chloride > bromide > perchlorate > iodide > nitrate. The data obtained are important for the diagnosis, prediction and analysis of corrosion processes due to the breakdown of sputtered coatings on M2 steel in diverse environments.

1. Introduction

High speed steels are widely used for the fabrication of tools and drills. Wear-resistant hard coatings are often applied on these substrates, and it is important that they also exhibit adequate corrosion resistance. Investigation of the corrosion process and corrosion rate of the steel substrate in diverse situations provides data which, together with data on the electrochemical behaviour of the coating, can be useful in developing diagnostic criteria for coating breakdown. Nevertheless, studies of the corrosion of these steels are, to our knowledge, not available in the literature.

In this work, the corrosion of M2 steel, a high speed steel obtained through powder metallurgy technology, has been studied. Annealing, quenching and tempering processes follow manufacture in order to produce high hardness and high toughness through changes in the microstructure [1–3].

Corrosion potential measurements, voltammetric techniques and electrochemical impedance measurements have been employed to study the corrosion process in aqueous environments containing a number of different inorganic salts of sodium and potassium in varying concentration. The reproducibility of the results obtained has been tested, and localized corrosion phenomena investigated.

2. Experimental details

Electrodes, of area 0.8 cm^2 , were prepared from discs of heat-treated M2 high speed steel (6.4% W, 5.0% Mo, 4.2% Cr, 1.9% V, 0.9% C by weight) by attaching a wire to the rear and covering with epoxy resin, leaving just one face exposed. They were polished down to $1 \mu\text{m}$ particle size with diamond lapping compound on a polishing cloth. Solutions in the concentration range 0.01–0.10 M containing chloride, bromide, iodide, nitrate, sulfate and perchlorate salts of sodium and potassium were prepared using

Millipore Milli-Q water (resistivity > $18 \text{ M}\Omega \text{ cm}$); the pH of these solutions was measured and was within the range 5.0–5.5.

A three-electrode cell containing a Pt foil auxiliary electrode and saturated calomel reference electrode was employed, controlled by a EG&G PAR273A potentiostat or, for impedance experiments, by a Solartron 1250 frequency response analyser with a model 1286 electrochemical interface.

Scanning electron microscopy was carried out on a Jeol T330 SEM equipped with a 'tracor chemical microanalysis' accessory.

3. Results and discussion

3.1. Corrosion potential

Corrosion potential measurements for M2 steel immersed in solutions of the different salts showed initial, sharp variations towards more negative values, the rate of change diminishing and stabilizing after several hours. Examples of the variation of E_{cor} with time are given in Fig. 1. After a certain time there is a (usually) small transient variation of potential in a positive direction superimposed on the the general negative trend in E_{cor} which can be associated [4] with the creation of pits in the surface, see Fig. 1, referred to as the pitting induction time. Subsequent large period oscillations superimposed on the general trend in E_{cor} , if it occurs, can be explained as corresponding to dissolution/passivation cycles of the films formed in the interior of the pits. Such oscillations in potential are particularly evident for potassium iodide and sodium perchlorate solutions, with periods of the order of 100 min. Figure 2 shows induction times for pit initiation and corrosion potential values after 21 h, the latter corresponding to the situation when the rate of change of E_{cor} with time has reached a steady value. Induction times are plotted in Fig. 2(a) with error bars based on three determinations, reflecting variations in the surface structure of the samples and the stochastic nature of pitting corrosion

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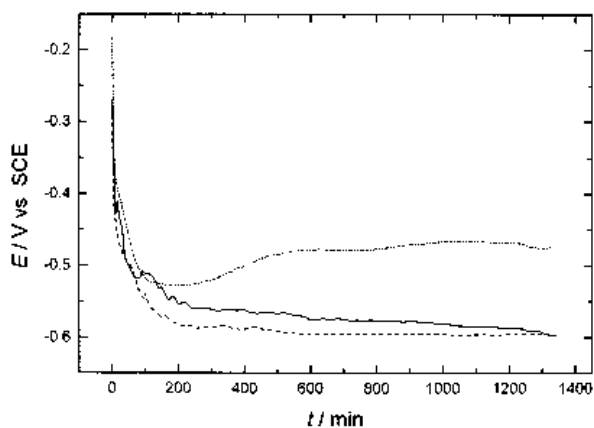


Fig. 1. Variation of corrosion potential, E_{cor} , of M2 steel with time in (—) 0.1 M KBr, (- - -) 0.1 M KCl and (—) 0.1 M KNO₃ electrolytes.

[5, 6]. A good correlation between the trends in induction times and E_{cor} values is clear by comparison of Fig. 2(a) and (b), showing that the E_{cor} values are determined mainly by localized corrosion phenomena.

The largest changes from initial values correspond to solutions containing sulfate and chloride ions. A general analysis of the differences caused by the various electrolytes shows little influence of the cation; after sulfate and chloride anions are bromide, iodide and perchlorate. Data for other steels, such as for stainless steels, show that chloride ions are the most aggressive ions (e.g. [4]), but sulfate, similar to other anions, has an inhibiting effect (e.g. [7, 8]). Thus the

results obtained in this study must be due to the different structure of high speed steel, including, with respect to stainless steels, the higher carbide content. This point will be further addressed below in the context of microscopy observations.

Nitrate anion, see Fig. 1, showed interesting behaviour and which was different from the other anions in that, after approximately 2 h immersion, the open circuit potential, instead of continuing to become gradually more negative, became more positive and then remained almost constant: this indicates that repassivation of the steel surface is occurring. Such behaviour was more pronounced the higher the nitrate concentration, suggesting that nitrate acts as an oxidizing agent shifting the corrosion potential to more positive values.

It was found in a previous study concerning the effect of chloride anion concentration on pitting susceptibility of various metals and alloys, that both the pitting potential, E_{pp} , and the induction time, t_i , are functions of chloride concentration [4]. The variation can be expressed by

$$E_{\text{pp}} = A + B \log [\text{Cl}^-] \quad (1)$$

$$\log t_i = C + D \log [\text{Cl}^-] \quad (2)$$

where A , B , C and D are constants, assuming constant temperature and pH. This relationship was tested for M2 steel using potassium chloride solutions in concentrations between 0.005 M and 0.10 M and led to a value for D of -0.29 . Note that in the case of AISI304 SS the value found was -0.58 [4]; however, in that case the induction time was much longer, of the order of hundreds of hours, so that a greater dependence on chloride concentration in that case is reasonable.

3.2. Potentiodynamic experiments

Various potentiodynamic experiments were carried out to investigate the effect of the nature of the solution on voltammetric profiles. Data obtained by optimized fitting of experimental curves registered in linear polarization resistance and linear sweep voltammetry experiments are presented in Table 1. Comparing linear polarization resistance values, R_p , with Fig. 2, it seems that a less negative corrosion potential is associated with a higher polarization resistance. Fitting of the experimental Tafel plot data leads to the results shown and indicates that the corrosion current is also lower.

The Tafel slopes, b_c , for the reduction reaction range between 0.120 and 0.196 V decade⁻¹. Assuming that, for the pH values of the solution in question (5.0–5.5), almost all the reduction reaction is reduction of oxygen (oxygen has not been excluded from the solution), this suggests that the mechanism involves a one-electron rate-determining first step to give O₂⁻ (if, for example, $\alpha_c = 0.5$ and $n = 1$ then $b_c = 0.120$ V decade⁻¹ assuming a first order reaction) according to:

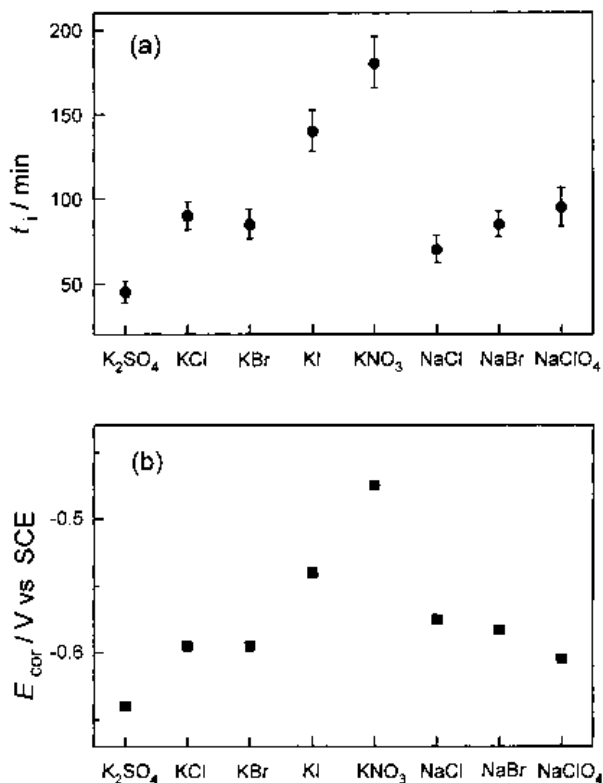
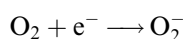


Fig. 2. (a) Induction time for pit initiation, t_i , and (b) corrosion potential, E_{cor} , after 1300 min. immersion in 0.1 M electrolyte solutions.

Table 1. Data obtained from linear polarization resistance and linear sweep voltammetry experiments

Solution	R_p /k Ω cm ²	I_{cor} /μA cm ⁻²	b_a /V(decade) ⁻¹	b_c /V(decade) ⁻¹
K ₂ SO ₄	1.11	15.87	0.142	0.294
KCl	1.88	7.43	0.141	0.184
KBr	2.07	6.45	0.151	0.196
KI	4.64	3.55	0.184	0.126
KNO ₃	5.71	2.86	0.157	0.125
NaCl	1.45	7.61	0.187	0.161
NaBr	2.13	6.41	0.206	0.158
NaClO ₄	2.34	5.11	0.193	0.156

Polarization resistance, R_p ; corrosion current, I_{cor} ; anodic and cathodic Tafel slopes, b_a and b_c



or alternatively involves an adsorption of intermediates which interact with iron species, the reduction of this adsorbed intermediate being the rds and leading to a reaction order of 1/2, as suggested previously for iron [9]. Our results do not permit us to distinguish the two cases. However, the appearance of values significantly higher than 0.120 V decade⁻¹ in some instances in Table 1 suggests a value of α_c less than 0.5 and the first of these two possibilities.

As discussed below, chemical microanalysis shows that in the anodic process iron in the M2 steel is preferentially oxidized, leaving the surface richer in the other components so that the b_a values predominantly reflect this oxidation. Thus, iron oxidation could occur in two ways: either in several steps with the first electron transfer rate determining or in one step with the low transfer coefficient value corresponding to an activated complex close to the zero oxidation state.

Cyclic voltammetry experiments, carried out after 10 min immersion in the test solutions, led to the determination of pitting and protection potentials, E_{pp} and E_{prot} , respectively. An example is shown in Fig. 3: from the E vs $\log I$ plots, E_{pp} is the potential at which the slope in the positive-going scan changes

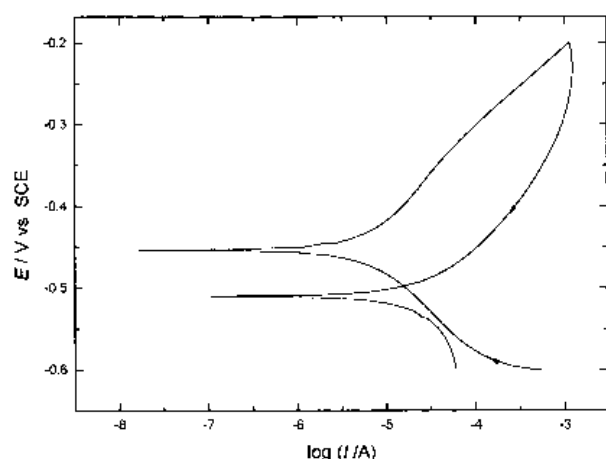


Fig. 3. Plot of E vs $\log I$ for cyclic voltammogram recorded in 0.1 M KCl after 10 min immersion; scan rate 2 mV s⁻¹.

and E_{prot} is the potential where the positive and negative going scans cross. The values obtained are shown in Fig. 4, the more positive potential corresponding to E_{pp} and the more negative to E_{prot} . The values can be clearly seen to be only slightly dependent on cation identity, but strongly dependent on the anion. Of particular interest is the fact that with bromide ion the protection potential value is so negative, the difference between E_{pp} and E_{prot} being much greater than for chloride or iodide ions. The obvious deduction is that bromide ions have difficulty in adsorbing on the surface or forming salts to inactivate the pits, but it is not clear why this should be, or to what extent it is dependent on steel composition.

The expression in Equation 1 was tested with potassium chloride solution and a value of -0.11 V was obtained for the constant B. Other steels for which the expression has been evaluated lead to values of: AISI 304SS -0.15 V [4], AISI 316SS -0.15 V [10], Fe-19Cr-8Ni -0.16 V [10], Fe-18Cr-8Ni -0.088 V [11] and pure iron -0.064V [12]. The value of -0.11 V is thus in good agreement with that obtained with other steels. It was also evident that the difference between pitting and protection potentials increased with increasing chloride concentration, both of these parameters moving towards more negative values, as would be predicted for systems subject to pitting corrosion.

3.3. Potential step experiments

Some potential step experiments were conducted from values of applied potential close to the open circuit potential after 30 min immersion to values between 0.1 V and 0.3 V more positive, in order to ascertain the influence of any differences between the anions in solution on the current transients. The registered transients were analysed according to a power law of the type $I \propto t^n$. An example of the results obtained is shown in Fig. 5.

It was found in all cases that the initial variation of the current followed Cottrellian diffusion law, $I \propto t^{-1/2}$. For small potential steps and for nitrate ion

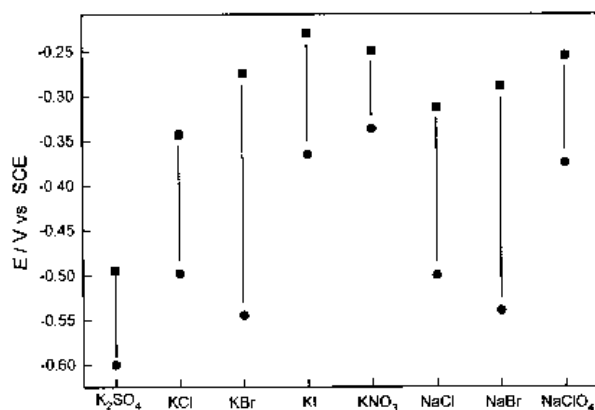


Fig. 4. Pitting (■) and protection (●) potentials as a function of electrolyte composition in 0.1 M solutions.

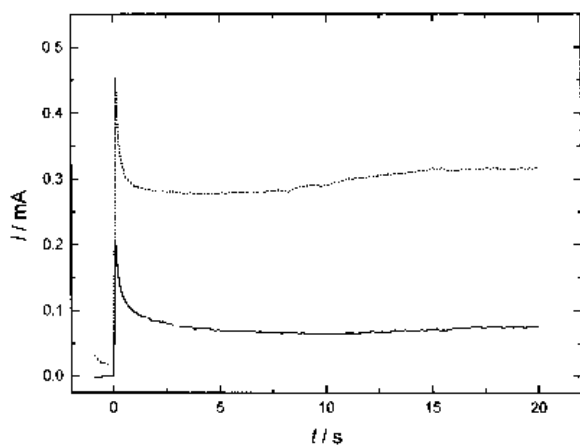


Fig. 5. Current transients obtained after potential steps of (—) +0.1 V and (---) +0.2 V from E_{cor} at electrode immersed in 0.1 M NaCl for 30 min.

even with 0.3 V steps, the current then became independent of time. This can be explained as corresponding to growth of an unstable oxide layer which can flake off of the surface [13]; this was observed visually. In bromide, chloride and sulfate solutions for step amplitudes of ≥ 0.2 V the current began to rise again after about 2 s following $I \propto t^{1/2}$, which can be explained through diffusion controlled dissolution in the pits [14]. In the case of sulfate-containing solutions, apart from higher currents after the initial decay period, oscillatory behaviour occurred for a 0.1 V potential step, suggesting cyclic pit birth and

death processes; at more positive potentials this largely disappeared and the current rose linearly with $t^{1/2}$ as for the other anions.

The results obtained with this technique were in good agreement with those obtained through corrosion potential and potentiodynamic sweep measurements.

3.4. Electrochemical impedance

Electrochemical impedance spectra, see example in Fig. 6, were registered after 15 min immersion at the open-circuit potential and 30 mV more positive for each of the solutions. The general form of the spectra was similar for all solutions. Such behaviour has been modelled in [15] assuming at the high frequency limit that the interface behaves as a homogeneous conductor, whereas at the low frequency limit the interface consists of small conducting areas (the pits) in an insulating plane (oxide film). A simplified model of a parallel RC circuit was proposed in which R represents the pit ohmic resistance and C the corresponding capacitance.

Thus, following this type of model and neglecting the low frequency limit, fitting of the spectra was possible by using a model of the interface considering two parallel pathways. The microscopic roughness of the electrode surface led to the necessity of using constant phase elements such that the simulation circuits contained one or (in the case of sulfate anion, the

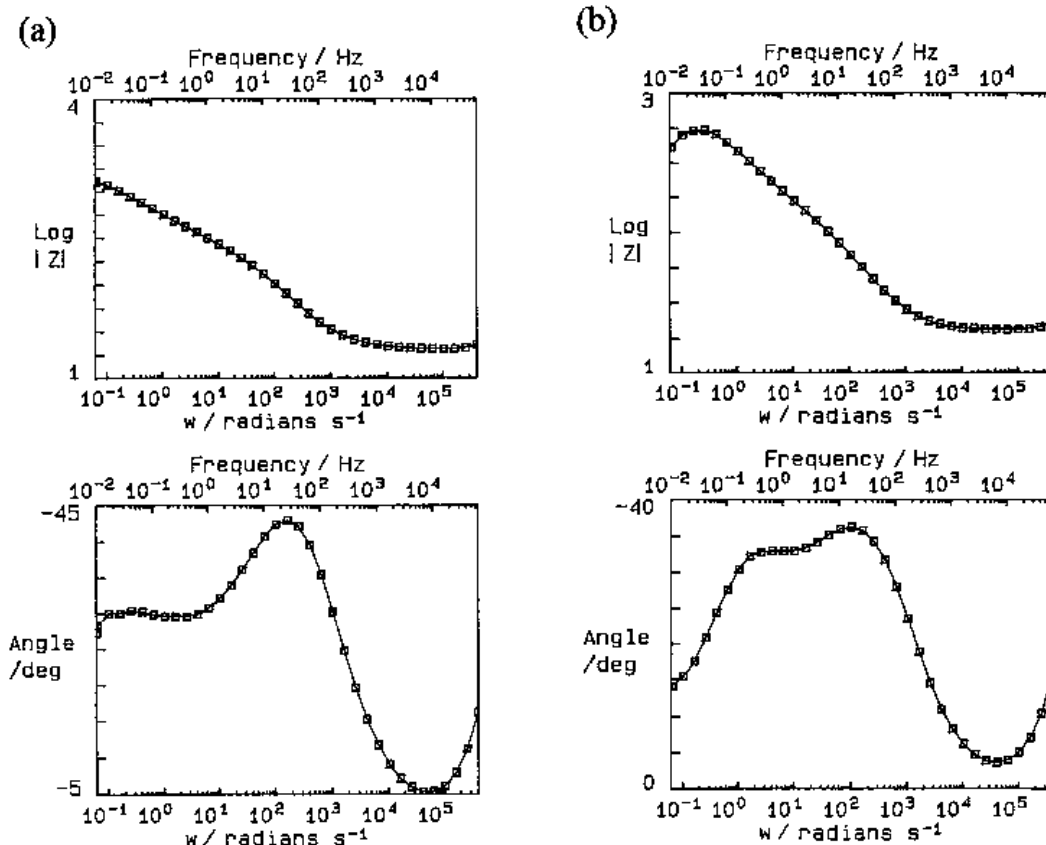


Fig. 6. Bode plots from electrochemical impedance experiments, exemplified by 0.1 M KCl solution after 15 min immersion. (a) Open circuit potential; (b) open circuit potential +30 mV.

most aggressive) two constant phase elements. This suggests that corrosion in the presence of the sulfate ion caused a more complex surface with pits and with areas of the surface which were either not visibly corroded or were corroded in a uniform fashion.

3.5. Microscopy observations

Optical microscopy and scanning electron microscopy with chemical microanalysis of the corrosion products was carried out for samples corroded in the most aggressive media, 0.1 M K_2SO_4 and 0.1 M KCl solutions. Large pits were obtained after immersion for 24 h, Fig. 7, and visual observation supports deductions made from impedance spectra. From sulfate solution large shallow pits (diameter up to 200 μm) with cracking of the surface layers within the pit were generally obtained. In the case of chloride solution, pits were deeper and smaller (diameter up to 40 μm), generally with a raised bump in the middle. Microanalysis showed that in both solutions iron was preferentially oxidized within the pits, with debris rich in iron spread out around the edge of the pit on top of the polished surface, presumably iron oxide.

The multiphase structure of heat-treated high speed steel [3] should be borne in mind in explaining these phenomena. Note that the composition of M2 steel in at% is 87.1% Fe, 2.1% W, 3.1% Mo, 2.2% Cr, 1.0% V, 4.5% C. Heat-treated M2 steel contains tempered martensite (a highly distorted α -iron structure with appreciable defect concentrations), primary

carbide phases, up to 4 μm diameter, which are not dissolved during annealing, and smaller particles ($\leq 0.4 \mu m$) of secondary carbides. The carbide entities provide hardness without compromising ductility. All of the alloying elements, except for a tiny fraction and some chromium which is soluble in martensite, are present in the carbide phases. The principal general difference from other steels is the existence of chromium carbide, mainly $Cr_{23}C_6$. It is probable that it is the martensite which pits leaving the carbide phases largely untouched, which would lead to a lower percentage of iron by chemical microanalysis.

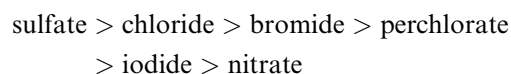
Pit density was greatest for sulfate-containing solutions followed by chloride, which is the main reason for the larger corrosion rate in sulfate solution. As remarked in Section 3.1, for many steels, particularly stainless steels, sulfate has an inhibiting effect on pitting corrosion in chloride solution (e.g. [4]). The different behaviour must be due to the steel microstructure. Many steels are of low carbon content and with larger amounts of alloying elements: the microstructure contains microphases of intermetallic compounds. Alternatively, they may have a similar carbon content but without the existence of chromium carbides. A full understanding of these phenomena needs a systematic study of different steels after different and carefully controlled heat treatments.

3.6. Comparative remarks

General analysis of the experimental data shows the influence of the anion identity on the corrosion rate and corrosion mechanism. The effect of the cation being sodium or potassium is very small: solution conductivities were measured with a conductivity cell, and observed differences between potassium and sodium electrolytes can be attributed to differences in conductivity.

In the presence of sulfate, chloride, bromide and perchlorate there is significant pitting corrosion, observed electrochemically and through microscopic visual observation. In the case of iodide ion, the corrosion rate is much lower but experimental evidence obtained from current-voltage profiles and impedance plots points to an identical mechanism. Concerning nitrate anion, some oxidizing agent effects arise, although the pitting potential still has a similar value.

Thus, based on all the experimental results, a general order of anion aggressivity in these type of aqueous media towards M2 steel can be written as



This order reflects anion charge density and anion size, with polarizability also having some influence. The only exception is perchlorate anion, the reason for which is not clear; however, as an anion it does show evidence of specific interactions with charged surfaces which are different from those of other singly-charged anions (e.g. [16]).

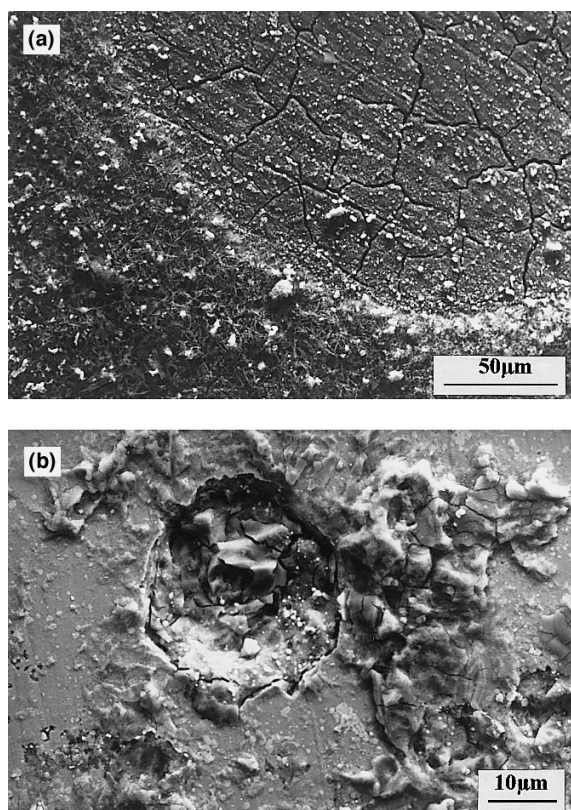


Fig. 7. SEM showing pits obtained after 24 h immersion at open circuit in solutions of (a) 0.1 M K_2SO_4 and (b) 0.1 M KCl.

4. Conclusions

Electrochemical techniques and scanning electron microscopy have been used to investigate the influence of different anions in solution on the corrosion of M2 high speed steel. All electrochemical results lead to the same conclusion that the corrosion rate is markedly affected by the identity of the anion. This aggressivity order is

sulfate > chloride > bromide > perchlorate
> iodide > nitrate

for the ions tested. Some special effects from nitrate ion were encountered, particularly in corrosion potential measurements.

High-speed steel is often used as substrate for wear-resistant sputtered coatings. The data obtained in this study are useful for developing diagnostics of coating breakdown in diverse environments and to aid in predicting which environments lead to high rates of corrosion, should breakdown occur.

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