The corrosion behavior of 70/30 copper-zinc alloy under the biofilm of sulfate-reducing bacteria

Korrosionsverhalten einer 70/30 Kupfer-Zink-Legierung unter dem Biofilm sulfatreduzierender Bakterien

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A laboratory study was carried out on the effect of the biofilm of sulfate-reducing bacteria (SRB), which plays an important role in corrosion of 70/30 copper-zinc alloy in culture media under anaerobic condition. The API medium was used to culture the SRB in Zhongyuan oilfield. Potential/time measurement showed that the presence of SRB makes the corrosion potential more active with SRB growth metabolite. Electrochemical impedance spectroscopy (EIS) was used to analyse the electrode process of 70/30 Cu-Zn alloy with SRB biofilm. Scanning electron microscopy (SEM) examinations revealed the formation of biofilm and corrosion products during exposure to SRB-containing culture medium. X-ray diffraction and EDS were used to analyse the corrosion products. The results show that the variation of activity of the SRB biofilm changes with SRB growth by the linear polarization resistance (R_p) and the EIS in culture medium inoculated SRB.

Eine Laborstudie wurde zum Einfluss des Biofilms sulfatreduzierender Bakterien (SRB) durchgeführt, die bei der Korrosion der 70/30 Kupfer-Zink-Legierung in Kulturmedien unter anaeroben Bedingungen eine große Rolle spielen. Das API Medium wurde verwendet, um die SRB im Zhongyuan Ölfeld zu züchten. Potential-Zeit-Messungen zeigten, dass die Anwesenheit von SRB das Korrosionspotential durch das Wachstum von SRB-Stoffwechselprodukten aktiver machte. Um den Elektrodenprozess der 70/30 Cu-Zn-Legierung mit SRB-Biofilm zu analysieren, wurde die elektrochemische Impedanzspektroskopie (EIS) eingesetzt. Rasterelektronenmikroskopische Untersuchungen zeigten die Bildung von Biofilm und Korrosionsprodukten während der Auslagerung in SRB-enthaltenem Kulturmedium. Röntgenbeugung und EDS wurden eingesetzt, um die Korrosionsprodukte zu analysieren. Die Ergebnisse bezüglich linearem Polarisationswiderstand (R_p) und EIS in mit SRB geimpftem Kulturmedium zeigten, dass die Aktivität des SRB-Biofilms sich mit dem Wachstum der SRB ändert.

1 Introduction

The role of microorganisms in the corrosion of metals and alloys has received much attention in recent years. The term microbiologically influenced corrosion (MIC) refers to increased corrosion caused by the presence and activities of microorganisms within biofilms on metal surfaces [1, 2]. MIC can be divided into two subsets: (1) microbiologically intermediated corrosion caused by chemical intermediates produced by microorganisms which are not in direct contact with the corroding surface and (2) MIC caused by chemical species generated within a biofilm at a metal/biofilm interface [3]. It has been known that sulfate-reducing bacteria (SRB) are the most important microorganisms in anaerobic MIC. SRB utilize sulfate ions ($S0_4^{2-}$) in the water, as an alternative to oxygen, as the terminal electron acceptor with reduction to sulfide ions (S^{2-}) during metabolism. SRB may cause corrosion by a variety of mechanisms, including the classical cathodic depolarization theory, or more likely by the direct corrosive effect of the sulfides produced [4].

Copper and copper alloys have been used frequently in culture medium heat exchangers due to their good corrosion resistance, mechanical workability, excellent electrical and thermal conductivity, and resistance to biofouling. The corrosion resistance of these alloys has been attributed to the formation of a protective film of cuprous oxide (Cu_2O) [5]. The protective film retards both the anodic dissolution of the alloys and the rate of oxygen reduction [6]. Therefore, it is not surprising that failure is always associated with the deterioration of the protective film. The deterioration mechanisms can be mechanical, as in cases of erosion-corrosion where the hydrodynamic regime probably disrupts the passive layer, or they can be chemical, when the culture medium coolant is contaminated [7, 8].

In spite of the well-documented antifouling properties of copper and copper alloys, it has recently been demonstrated that these alloys are vulnerable to biocorrosion. The culture medium in shore and industrial pollutants from refineries, power plants, offshore oil rigs, petrochemical plants, oil tankers, commercial ships and raw sewage, corroded copper and copper alloys. Thus, there is significant interest in understanding the microbial corrosion behavior of copper alloys, the purpose of this work was to investigate the effects resulting from the combined presence of biofilms and sulfides produced by SRB on the corrosion behavior of 70/30 Cu-Zn alloy.

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2 Materials and methods

2.1 Microorganisms

SRB, belong to Desulfovibrio vulgoris [9], come from Zhongyuan oil field sewage.

2.2 Culture medium and culture condition

SRB can grow in culture medium and culture condition recommended by API RP-38 [10], Static batch culture medium for experiment contained (g/l-distilled water): sodium lactate, 4.0 ml/l; yeast extract, 1.0 ml/l; vitamin C, 0.1 g/l; $MgSO_4 \cdot 7H_2O$, 0.2 g/l; K_2HPO_4, 0.01 g/l; $CaCl_2$ 0.1 g/l; NaCl, 10.0 g/l; $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, 0.2 g/l. The pH of culture medium was adjusted to 7.2–7.5 using 1M HCI or 1M NaOH before autoclaving and readjusted after autoclaving if required. The medium was sterilized in autoclaving at 1.4 kg/cm^2 in 20 min, and then cooled at room temperature nitrogen. When the medium was cold, 0.2 g $FeSO_4 \cdot (NH_4)SO_4 \cdot 6H_2O$ sterilized with ultraviolet ray has been added in.

2.3 Electrochemical studies

The material used for this investigation was 70/30 copper-zinc alloy and the chemical composition is given in Table 1. Approximately 10 mm long, 10 mm diameter brass rod, was fixed using an epoxy resin and was used as working electrode. Platinum electrode was used as counter, while a saturated calomel electrode (SCE) was used as a reference. The test cell contained six specimen holders for electrochemical measurements and two racks on the sides for immersion tests. The cells also had inlets for counter and reference electrodes and a gas bubbler. The electrode surfaces were mechanically ground with emery papers of different grits and polished with emery paper up to grit 1200. The specimens were degreased in acetone, rinsed with deionized water and air dried before testing.

The study included open-circuit corrosion potential, linear polarization resistance (R_p), and electrochemical impedance measurements as well as morphological examinations of the mode of corrosion attack. The corrosion potential and R_p measurements were made as a function of time for a period of 14 days, while the impedance measurements were made after different exposure periods. The polarization experiments were conducted using a computerized corrosion measurement system. Linear polarization was performed by polarizing the specimens potentiostatically 20 mV in the anodic and cathodic directions after 1 h of immersion and after 14 days of immersion. The impedance measurements were made using a sine wave voltage with an amplitude of 10 mV.

2.4 Surface analysis of biofilm and corrosion products

For morphological studies, after 30 days at 37 ± 1 °C, the alloy coupons covered with biofilm were removed from culture medium, washed using distilled water, dehydrated in a graded series of alcohol solution (dehydrated 10 minutes in 50, 70, 80, 90, 95% alcohol solution, 30 min in 100% alcohol.). The mode of corrosion was assessed after ultrasonic cleaning in acetone. And then natural dried under nitrogen and examined using scanning electron microscopy (SEM).

Table 1. Composition of 70/30 copper-zinc alloy
Tabelle 1. Zusammensetzung der 70/30 Kupfer-Zink-Legierung

Element	Cu	Zn	Pb	Fe	Sb	Bi	P
Wt%	69.91	29.93	0.04	0.11	0.004	0.002	0.001

The corrosion products were also analyzed using energy dispersion spectroscopy (EDS) and X-ray diffraction (XRD).

3 Results and discussion

3.1 Open-circuit potential measurements

Fig. 1 shows the changes in open-circuit corrosion potential as a function of exposure time for 70/30 Cu-Zn alloy in sterile culture medium and in culture medium inoculated with SRB. It can be seen from Fig. 1 that the free corrosion potential is generally much more noble in sterile culture medium than in the presence of SRB. In culture medium inoculated with SRB, the corrosion potential undergoes an initial potential drop and is followed by a gradual shift towards more noble values. At the end of testing, the corrosion potential is about −280 mV in sterile culture medium, while it is about −520 mV in the presence of SRB; a difference of 240 mV.

3.2 Linear polarization measurements

Fig. 2 shows that the corrosion rate of 70/30 Cu-Zn alloy decreased rapidly during the first 2 days of exposure to sterile culture medium and then gradually stabilized under a steady state of 86.8 (Mohm)$^{-1}$.cm^{-2}. In the presence of active SRB, the corrosion rate decreased rapidly to 54.5 (Mohm)$^{-1}$.cm^{-2} during the first 2 days of exposure, but then gradually increased to, reaching a value of 260 (Mohm)$^{-1}$.cm^{-2} at the end of testing. These results indicate that the presence of

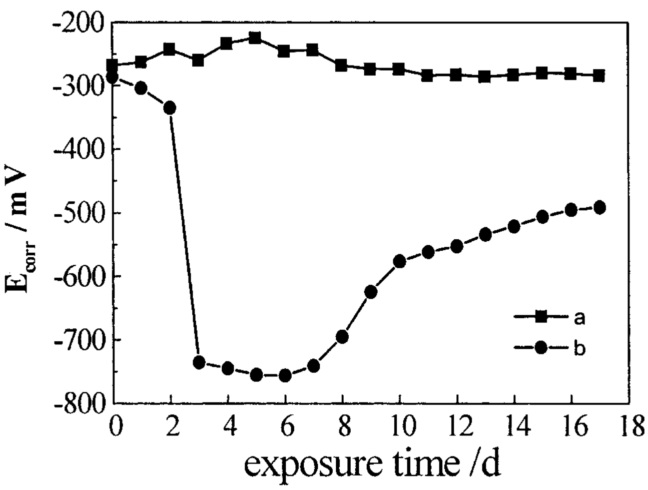

Fig. 1. Free corrosion potential versus exposure time for 70/30 Cu-Zn alloy in culture media in the absence and presence of SRB, (a) sterile, (b) SRB inoculated

Abb. 1. Freies Korrosionspotential als Funktion der Auslagerungszeit für die 70/30 Cu-Zn-Legierung in Kulturmedien mit und ohne SRB, (a) steril, (b) mit SRB geimpft

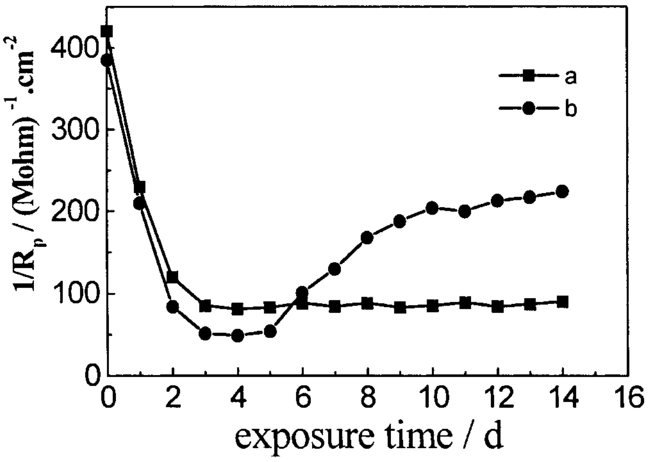

Fig. 2. $1/R_p$ versus exposure time for 70/30 Cu-Zn alloy in culture media in the absence and presence of SRB, (a) sterile, (b) SRB inoculated

Abb. 2. $1/R_p$ als Funktion der Auslagerungszeit für die 70/30 Cu-Zn-Legierung in Kulturmedien mit und ohne SRB, (a) steril, (b) mit SRB geimpft

SRB increases the corrosion rate of the alloy by 3 times. The present results obtained under free corrosion condition indicate that there was an increase in the corrosion rate accompanied by a shift of potential in the active direction when 70/30 Cu-Zn alloy was exposed to culture medium inoculated with SRB. Thus, the activation of the corrosion potential observed in the present work could be attributed to the enhancement of the anodic process. This is consistent with the activation of the corrosion potential upon exposure to polluted culture medium which has been previously reported for A1-brass [11], Monel 400 [11], and 70/30 Cu-Ni [12].

The relatively noble free corrosion potential and the low corrosion rate attained in sterile culture medium reflecting the protective film of the alloy did not be damaged. Under this condition, the material did not suffer from corrosion products, while it experienced pitting attack in the culture medium inoculated SRB. This behavior indicated that a series of acidic metabolite (propanoic, benzoic, et al) had been produced in the process of SRB growth and metabolism. The acidic metabolite let the pH of solution fall from original 7.5 to 6.0 and eroded primary biofilms, and that formed complex biofilms (black, porous, sulfur-containing corrosion products), accelerated corrosion of 70/30 Cu-Zn alloy.

3.3 Impedance measurements

The impedance response of 70/30 Cu-Zn alloy in culture medium in the absence and presence of SRB is shown in Fig. 3 for data obtained after 1 h, 3 days and 14 days of exposure. In the presence of SRB, the impedance of the material in culture medium inoculated with active SRB is seen to increase first and then decrease across a large frequency domain increasing the exposure time of 70/30 Cu-Zn (Fig. 3a). This decrease was associated with an decrease in the phase angle peak and its shift towards lower frequencies (Fig. 3b). This behavior is quite expected as it reflects the formation and damage of a protective film on the metal surface. These later changes suggest that the presence of bacteria damages a protective film formed firstly and accelerates corrosion of the alloy.

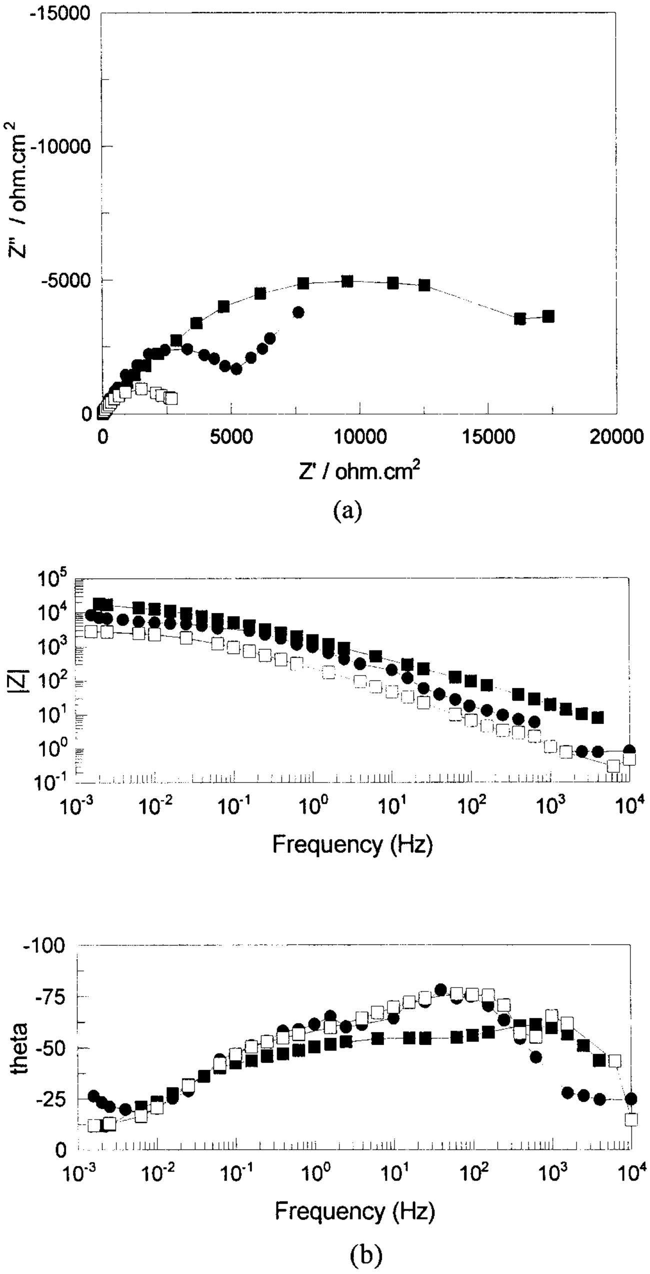

Fig. 3. EIS (a) and Bode plots (b) of Cu-Zn alloy at different time in culture medium in the presence of SRB: (□) 1 h, (■) 3 days, (●) 14 days after inoculated with SRB

Abb. 3. EIS- (a) und Bode-Darstellungen (b) der Cu-Zn-Legierung zu verschiedenen Zeiten im Kulturmedium bei Anwesenheit von SRB: (□) 1 h, (■) 3 Tage, (●) 14 Tage nach Impfen mit SRB

3.4 Morphological examinations

70/30 Cu-Zn specimens immersed in sterile culture medium did not suffer any corrosion attack during the whole exposure period. In the presence of SRB, patches of corrosion product layer mixed with ferrous sulfide were seen (Fig. 4a). The formation of this layer was associated with the depletion of zinc and enrichment of copper and sulfur at the alloy surface. There were some crystals protruding on the surface of corrosion products (Fig. 4b). The crystals were cuprous sulfide (Cu_2S) testified by analysis of EDS (Fig. 5) and XRD

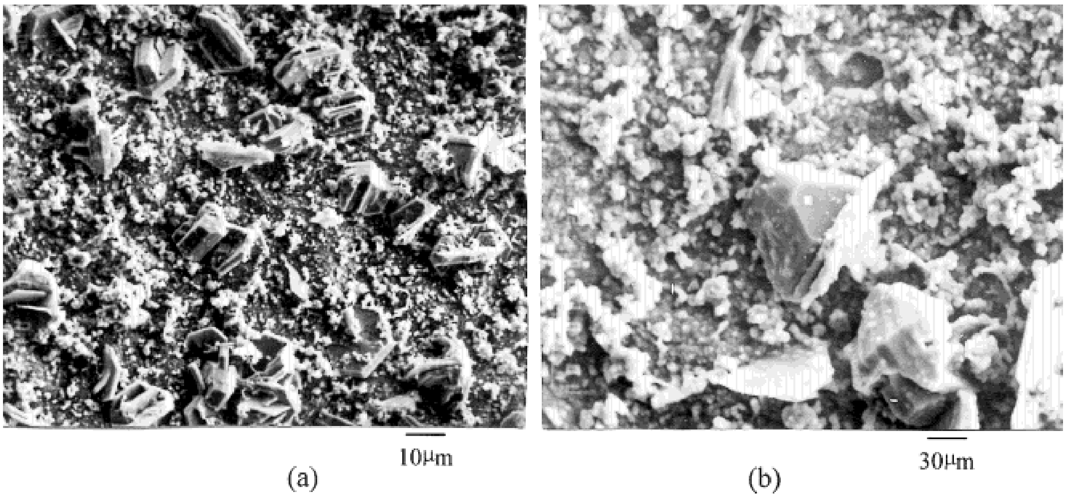

Fig. 4. SEM of corrosion products of 70/30 Cu-Zn alloy in culture medium inoculated with SRB

Abb. 4. REM-Aufnahmen der Korrosionsprodukte der 70/30 Cu-Zn-Legierung in Kulturmedium, geimpft mit SRB

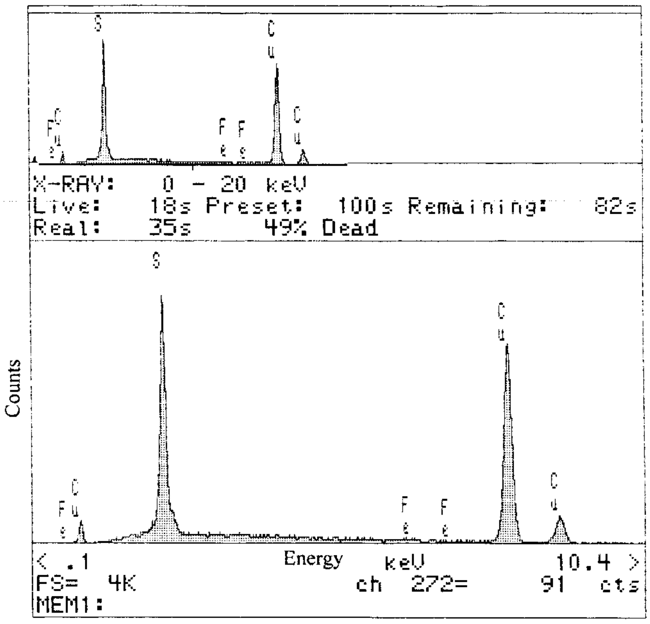

Fig. 5. EDS spectra of corrosion products of 70/30 Cu-Zn alloy in culture medium inoculated with SRB

Abb. 5. EDS-Spektren der Korrosionsprodukte der 70/30 Cu-Zn-Legierung im Kulturmedium, geimpft mit SRB

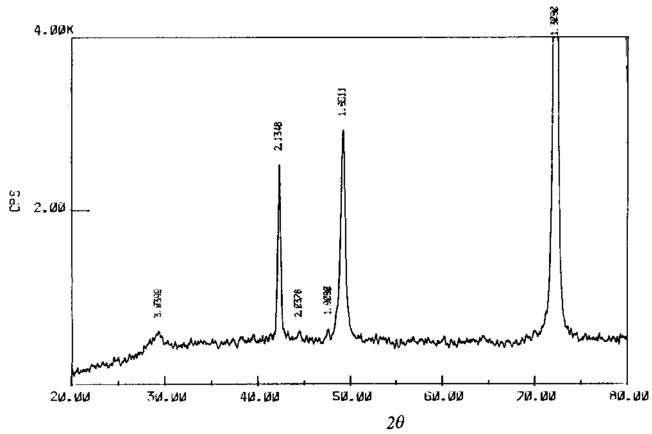

Fig. 6. XRD analysis of corrosion products of Cu-Zn alloy

Abb. 6. XRD-Analyse der Korrosionsprodukte der Cu-Zn-Legierung

(Fig. 6). When corrosion products were cleared away and the surface was reexamined after ultrasonic cleaning in acetone, it was found to have pitting holes of corrosion product (Fig. 7b). The phenomena analysis indicated that the surface of the material and inside the pits was depleted in zinc.

In the presence of bacteria, a corrosion product layer was formed, while a general form of corrosion and pitting occurred. All phenomena agree to indicate that a non-protecting layer is formed instead of the normal passive film. EDS analysis confirmed that a sulfide rich layer was formed after exposure to culture medium contaminated with active SRB in addition to the depletion of zinc. A similar behavior was reported by *Gomezde Saravia* et al. [12]. They found that uneven distribution of bacteria and their extracellular polymeric substance, combined with the corrosion products, reduced the protective characteristics of the outer layer. *Schiffrin* and *De Sanchez* [7] also reported that bacterial contamination led to the loss of passivity of copper alloys in culture medium. This was attributed to the long term modification of the oxide layer into a sulfide rich layer. The impedance response provided in Fig. 3 lends further support to the view that the presence of bacteria affects the formation of the normal protective film.

4 Conclusions

The free corrosion potential of 70/30 Cu-Zn alloy was more noble in sterile culture medium than in SRB-inoculated culture medium. The presence of SRB decreased the linear polarization resistance of the alloy.

With increasing the exposure time to culture medium inoculated with SRB, the impedance first increased and then decreased and presented two time constants. This behavior was attributed to the formation of an adherent corrosion pro-

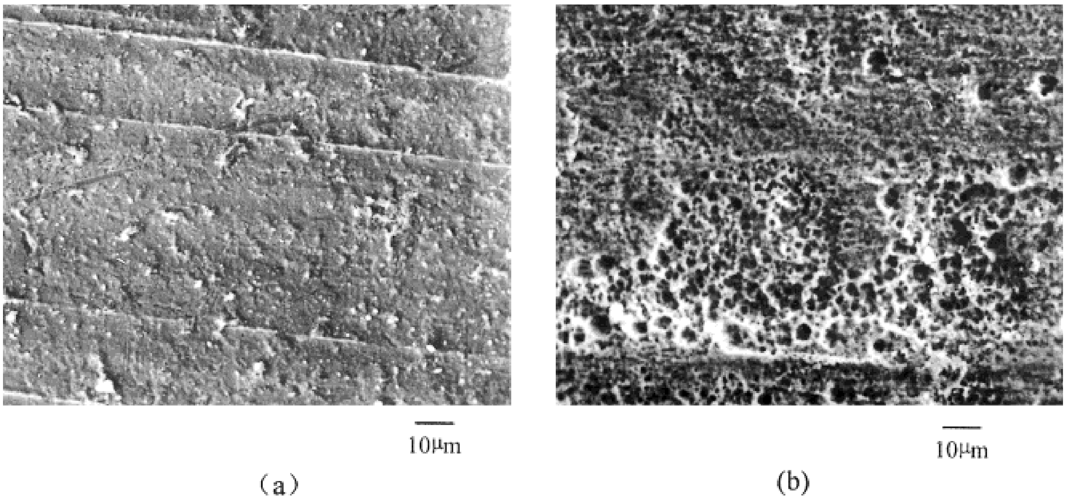

Fig. 7. SEM of the metal surface (a) sterile, (b) after corrosion products of 70/30 Cu-Zn alloy in culture medium inoculated with SRB were removed

Abb. 7. REM-Aufnahmen der Metalloberfläche (a) steril, (b) nachdem die sich im mit SRB geimpften Kulturmedium gebildeten Korrosionsprodukte der 70/30 Cu-Zn-Legierung entfernt wurden

duct layer and it was correlative with the structure of the SRB biofilm. When there existed the acidic substance produced by SRB, the primary biofilm became loosen, porous and lost its protection, and enhanced the corrosion of the alloy.

Morphological examinations revealed that a patchy layer of corrosion products mixed with bacteria was formed during exposure to culture medium inoculated with SRB. In presence of SRB, the corrosion product layer covered a larger area of the surface and became more adherent. Intergranular attack and micro pits were seen underneath and within the patches of corrosion products. The corrosion of the alloy was associated with depletion of zinc and enrichment of copper and sulfur at the surface.

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