

Effect of  $\beta$ -amino-alcohol derivative on the dezincification of 65-35

brass in simulated atmospheric water

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Tsinghua University, Beijing 100084, China**Abstract**

The influence of new inhibitor namely 1,3-bis-diethylamino- propan-2-ol (DEAP) on the dezincification of 65-35 brass in simulated atmospheric water has been studied by potentiostatic current transient measurement, solution analysis and surface evaluation techniques. Potentiostatic current transient results showed that the investigated compound can effectively retard the chemical dissolution of brass in simulated atmospheric water. Solution analysis revealed that the weigh loss of brass electrode remarkably decreased in the presence of DEAP, changing from  $7.375 \times 10^{-3}$  mg (blank) to  $9.567 \times 10^{-4}$  ( $10^{-2}$  M). The scanning electron microscope (SEM) and electron probe microanalyzer (EPMA) measurements showed that DEAP may better adsorb to zinc component than to copper component, inhibiting the dezincification of brass by the complexes film of  $\text{Zn}^{2+}$ -DEAP and  $\text{Cu}^{+}$ -DEAP. The nature of the protective film was characterized by an X-ray photoelectron spectroscope (XPS) analyzer.

**Keywords:** Corrosion; Inhibitor; Brass; Potentiostatic

## 1 Introduction

Brass is susceptible to dezincification corrosion in the caustic solution, which leads to the failure of its valuable physical and mechanical properties [1]. The preferential chemical dissolution of zinc component will result in a copper-rich porous structure and make the brass less against the attack of aggressive ions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Generally, the detrimental effects on the dezincification of brass can be minimized by the addition of organic compounds. The inhibition mechanism proposed for copper and its alloys was considered to be attributed to the chelating action of inhibitor molecules and the formation an effective adsorption film.

In the past 50 years, the use of organic compounds as corrosion inhibitors for copper and its alloys increased continually [2-5]. Numerous investigations on the corrosion inhibitors showed most effective organic inhibitors contained N, O and S atoms, which can co-ordinate with metal ions through the lone pair electrons to form a protective complex film, inhibiting the copper corrosion in the aggressive solution [6]. Telegdi et al. [7] have studied some azole derivatives referred as 5-mercapto-1-phenyl-tetrazole and 5-(4%-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole as corrosion inhibitor for copper in sodium sulphate and chloride solution, suggesting the investigated azole compounds exhibited good inhibition properties in caustic medium. Kosec et al. [8] studied the local corrosion of brass in chloride solution with benzotriazole. They concluded that the complex film composed of  $\text{Cu(I)-BTA}$  and  $\text{Zn(II)-BTA}$  are effective against brass corrosion in chloride solution. Mihit et al. [9] investigated the influence of some tetrazolic compounds on

the corrosion of brass in nitric acid solution. They suggested that the investigated compounds are mixed-type inhibitors without changing the mechanism of hydrogen evolution reaction. Ravichandran and Rajendran [10] studied the effect of N,N-dibenzotriazol-1-ylmethylaminomethane and N-[1-(benzotriazol-1-yl)ethyl]aniline on the corrosion and dezincification of brass in artificial seawater, revealing the addition of inhibitors can effectively retard the anodic dissolution by blocking the active sites of brass surface. Huynh et al. [11] reported the corrosion inhibition of octyl esters of carboxy benzotriazole on copper in an aerated sulfate solution.

Following the previous works concerning the application of 1,3-bis-diethylamino-propan-2-ol (DEAP) as corrosion inhibitor for brass [12,13], in this work, we give a further study on the dezincification of 65-35 brass in simulated atmospheric water with DEAP by potentiostatic current transient measurement, solution analysis and surface evaluation techniques, SEM, EPMA and XPS. We are interesting to find that DEAP may better adsorb to zinc component than to copper component, inhibiting the dezincification of brass in the aggressive medium.

## 2 Experimental

DEAP was synthesized according to the reported procedure [14]. The electrolyte was simulated atmospheric water composed of 0.1 g/L NaCl, 0.1 g/L NaHCO<sub>3</sub> and 0.1 g/L Na<sub>2</sub>SO<sub>4</sub>. Specimens were made from 65-35 brass with the following chemical composition (wt %): Cu 63.5~68.0; Fe 0.10; Pb 0.03; Sb 0.005; Bi 0.002; P 0.01, Zn balance. Potentiostatic current transient (PAR M173) tests were conducted in a traditional three-electrode cell by the applied potential of 300 mV under thin

electrolyte layer with the thickness of about 100  $\mu\text{m}$ . The exposed area of work electrode was 1  $\text{cm}^2$ . The equipment in this study was similar to that reported by R. P. Vera Cruz et al [15]. The amount of Cu and Zn ions leached out from electrode was determined by inductance coupling plasma (ICP) emission spectra method.

The protective film on brass surface without and with DEAP after gravimetric tests has been analyzed using scanning electron microscope (SEM), electron probe microanalyzer (EPMA) and X-ray photoelectron spectroscopy (XPS). The gravimetric measurement was done according to the JB/T 6071 standard.

### 3 Results and discussion

Brass corrosion in simulated atmospheric water produces  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  ions. The weight loss of brass electrode in the aggressive medium can be determined by ICP analysis. It is known that the dissolution rate of brass may involve long time in order to get a reproducible and stable condition. In this case, the corrosion process of brass in simulated atmospheric water was accelerated by potentiostatic current transient measurement.

Fig. 1 showed the current-time curves of brass under thin electrolyte layer without and with DEAP at  $10^{-2}$  M by the applied potential of 300 mV for 15 min. It was clearly that the corrosion current density of brass in the DEAP-containing aggressive medium decreased from 26.1  $\mu\text{A}/\text{cm}^2$  (blank) to 1.1  $\mu\text{A}/\text{cm}^2$  (DEAP), revealing that the chemical dissolution of brass in the solution has been effectively retarded. After potentiostatic tests, the solution was analyzed to determine the leaching characteristics of electrode. The obtained data by ICP was used to calculate the weight loss of

electrode which can be calculated by the following equation:

$$\Delta m = \sum C_i \times S$$

Where  $\Delta m$  and  $S$  represent weight loss and the exposed area of electrode,  $C_i$  is the concentration of cations in the solution, and  $i$  referred as  $\text{Cu}^+$  and  $\text{Zn}^{2+}$ .

After solution analysis, it was found that the weight loss of electrode was  $7.375 \times 10^{-3}$  mg in the blank solution, whereas the weight loss decreased to  $9.567 \times 10^{-4}$  mg with DEAP at  $10^{-2}$  M. This data indicated the investigated compound exhibited good inhibition performance for brass in simulated atmospheric water.

The gravimetric measurement was done according to the JB/T 6071 standard. After gravimetric tests, the specimens were analyzed by SEM, EPMA and XPS. Fig. 2 (a) showed the SEM image of the specimen in the absence of DEAP. It was evident that the specimen has been suffered severely local corrosion, presenting a grid-like characteristic. It was also found that lots of loosen corrosion products randomly distributed in the circular region, indicating the corrosion products were easy to leave from the metal surface and to develop stronger corrosion activity inducing less protective towards aggressive ions. Fig. 2 (b) showed the SEM image of the specimen in the presence of DEAP at  $10^{-2}$  M. We found that a compact protective film covered the metal surface almost completely, in agreement with the potentiostatic test which the inhibitor of DEAP presented good inhibition efficiency for brass.

Fig. 3 showed the EPMA analysis of the specimen in the presence of DEAP at  $10^{-2}$  M. A grid-like protective film was found in Fig. 3 (a), suggesting that DEAP chelated with copper/zinc and formed a protective layer on the brass surface. The grid-like film

was an indication that the protective film composed of  $\text{Cu}^+$ -complex and  $\text{Zn}^{2+}$ -complex, not the pure  $\text{Cu}^+$ (or  $\text{Zn}^{2+}$ )-complex. Figs. 3 (b) and (c) showed the circular region was composed of Zn component and peripheral domain was composed of Cu component. The most useful elements of N element (Fig. 3 (d)) were detected by the EPMA analysis, identifying the presence of DEAP in the protective film. In order to evaluate the preferential adsorption of DEAP on  $\text{Zn}^{2+}/\text{Cu}^+$  element in the adsorbed film, a single-line EPMA scan was measured across the sample area, which was shown in Fig. 3 (e). It was evident that the relative content of C in circular region was distinct higher than peripheral region, suggesting DEAP preferential co-ordinate with  $\text{Zn}^{2+}$  ions and form a compact  $\text{Zn}^{2+}$ -complex, inhibiting the dezincification process of brass in simulated atmospheric water.

In order to investigate the chemical states, the protective film was further analyzed by XPS spectra. Fig. 4 (a) showed the XPS narrow scan for Zn 2p. The Zn 2p peaks can be decomposed into two peaks at binding energies of 1021.6 eV ( $\text{Zn } 2p_{3/2}\text{-O}$ ) and 1044.7 eV ( $\text{Zn } 2p_{1/2}\text{-O}$ ), respectively, which were consistent with the literature values of ZnO [16]. It was interesting to find that there were also two characteristic peaks at higher binding energy (1021.9 eV and 1045.1 eV). The shift of ZnO peak was attributed to the formation of  $\text{Zn}^{2+}$ -DEAP complex. Fig. 4 (b) showed the XPS narrow scan for Cu 2p. The binding energy for Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  at 931.8 eV and 951.7 eV agreed with the data found in reference for cuprous oxide  $\text{Cu}_2\text{O}$  [17]. The  $\text{Cu}_2\text{O}$  peaks shifted about 0.7 eV toward higher binding energy, changing from 931.8 eV and 951.7 eV to 932.5 eV and 952.3 eV, was resulted in the formation of  $\text{Cu}^+$ -DEAP

complex. In Fig. 4 (c), N 1s band was detected at 399.6eV, identifying the presence of DEAP in the complex film, as nitrogen is present only in the DEAP molecule. Based on the above experimental data, we proposed that both complexes,  $\text{Zn}^{2+}$ -DEAP and  $\text{Cu}^{+}$ -DEAP, were composed of the protective film.

#### 4 Conclusions:

In this work, we have a further investigation on the dezincification of 65-35 brass in simulated atmospheric water. The experimental results indicated the addition of 1,3-bis-diethylamino-propan-2-ol (DEAP) can effectively retard the chemical dissolution of brass in simulated atmospheric water. We have found that weigh loss of brass electrode remarkably decreased in the presence of DEAP, changing from  $7.375 \times 10^{-3}$  mg (blank) to  $9.567 \times 10^{-4}$  ( $10^{-2}$  M). SEM, EPMA and XPS measurements revealed that DEAP may preferential adsorb to zinc component than to copper component, inhibiting the dezincification of brass by the complexes film of  $\text{Zn}^{2+}$ -DEAP and  $\text{Cu}^{+}$ -DEAP.

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**References**

- [1] Nagiub A, Mansfeld F. Corros Sci 2001; 43: 2147-71.
- [2] Qafsaoui W, Blanc C, Pebere N, Takenouti H, Srhiri A, Mankowski G. Electrochim Acta 2002; 47: 4339-46.
- [3] Walker R. Corrosion 2000; 56: 1211-19.
- [4] Abed Y, Kissi M, Hammouti B, Tabe M, Kertit S. Prog Org Coatings 2004; 50: 144-7.
- [5] Estevão LRM, Nascimento RSV. Corros Sci 2001; 43: 1133-53.
- [6] Abed Y, Kissi M, Hammouti B, Tabe M, Kertit S. Prog Org Coatings 2004;50:144-7.
- [7] Telegdi J, Shaban A, Kálmán E. Electrochim Acta 2000; 45: 3639-47.
- [8] Kosec T, Milošev I, Pihlar B. Appl Surf Sci 2007; 253: 8863-73.
- [9] Mihit M, Issami SE, Bouklah M, Bazzi L, Hammouti B, Addi EA, Salghi R, Kertit S. Corros Sci 2006; 252: 2389-95.
- [10] Ravichandran R, Rajendran N. Appl Surf Sci 2005; 239: 182-92.
- [11] Huynh N, Bottle SE, Notoya T, Schweinsberg DP. Corros Sci 2000; 42: 259-74.
- [12] Gao G, Liang CH. Corros Sci 2007; 49: 3479-93.
- [13] Gao G, Liang CH. J Electrochem Soc 2007; 154: C144-51.
- [14] Ludwig BJ, West WA, Farnaworth DW. J Am Chem Soc 1954; 76: 2891-3.
- [15] Vera Cruz RP, Nishikata A, Tsuru T. Corros Sci 1996;38:1397-406.
- [16] Woo JC, Kim GH, Kim JG, Kim CI. Surf Coat Technol 2008; 202: 5705-8.
- [17] Wang L, Wei G, Qi B, Zhou HL, Liu ZG, Song YH, Yang XR, Li Z. Appl Surf Sci



## Figures

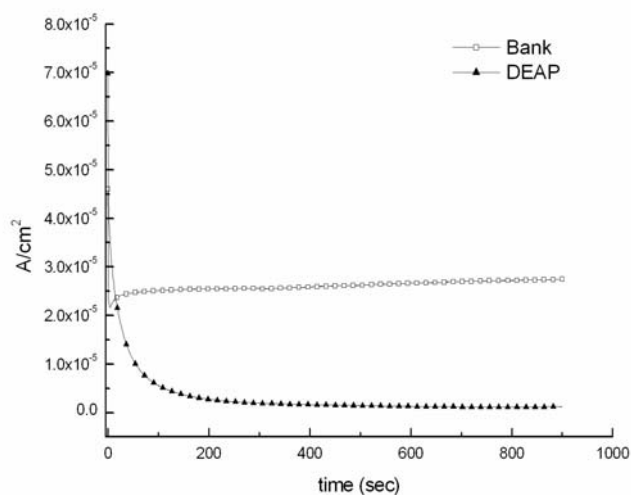


Fig. 1

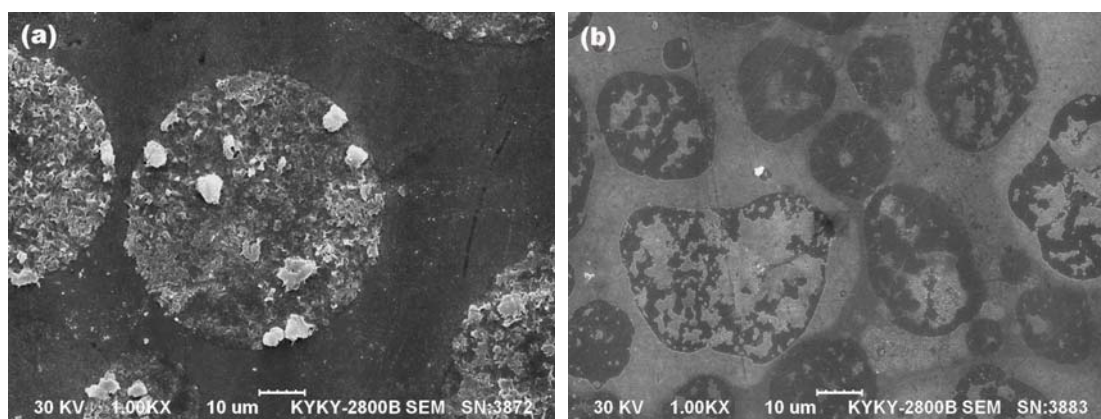
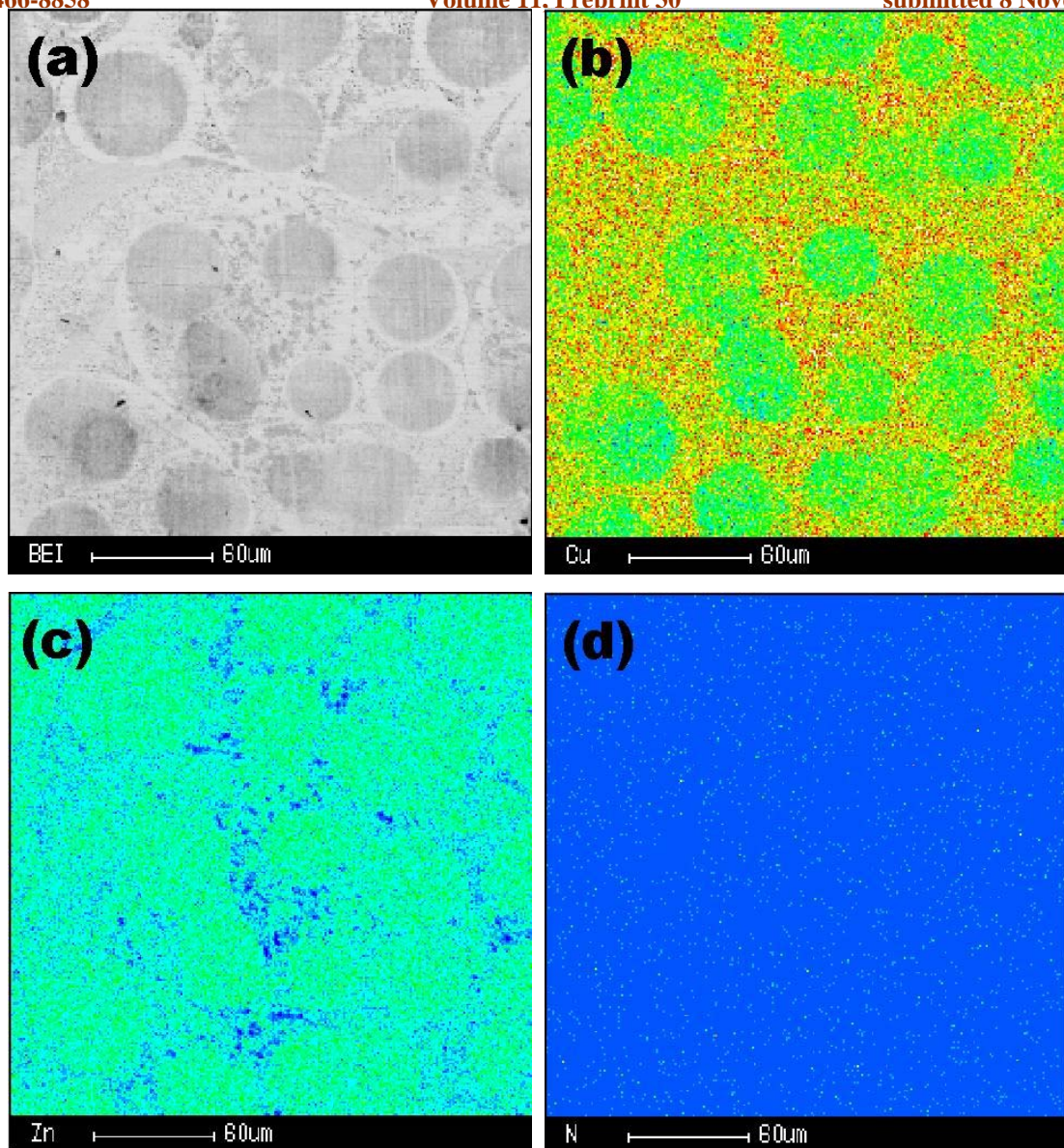


Fig. 2



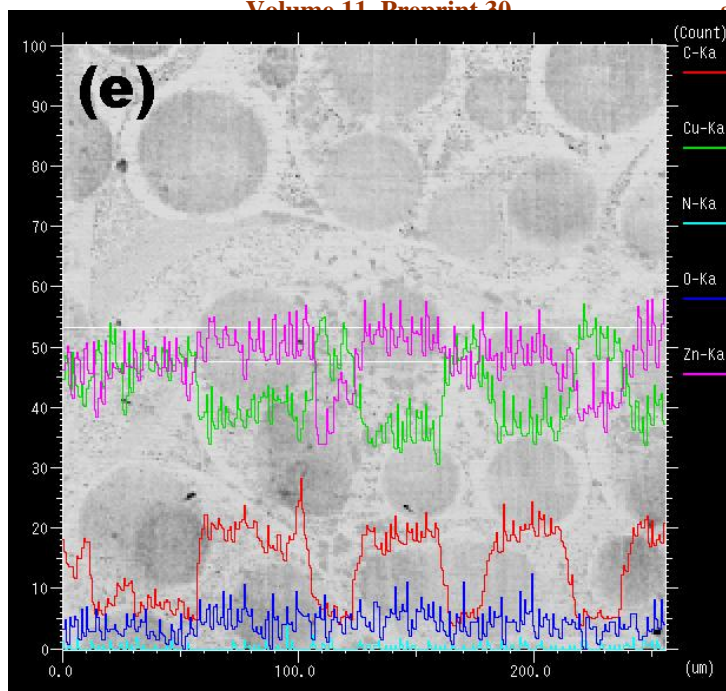
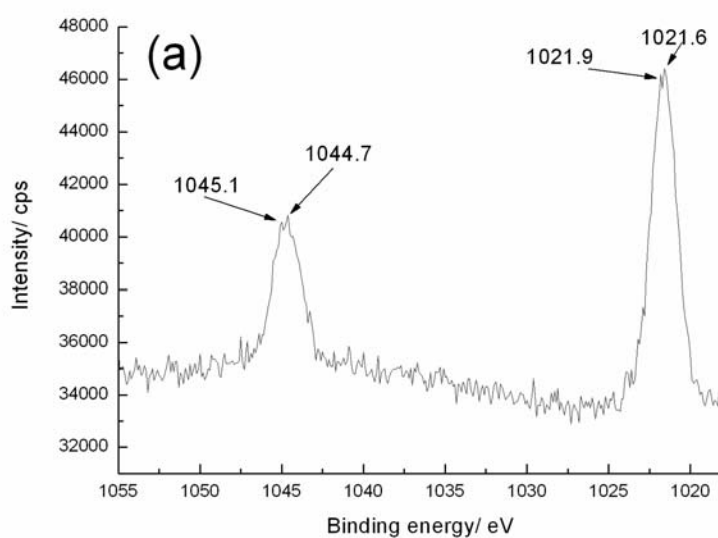


Fig. 3





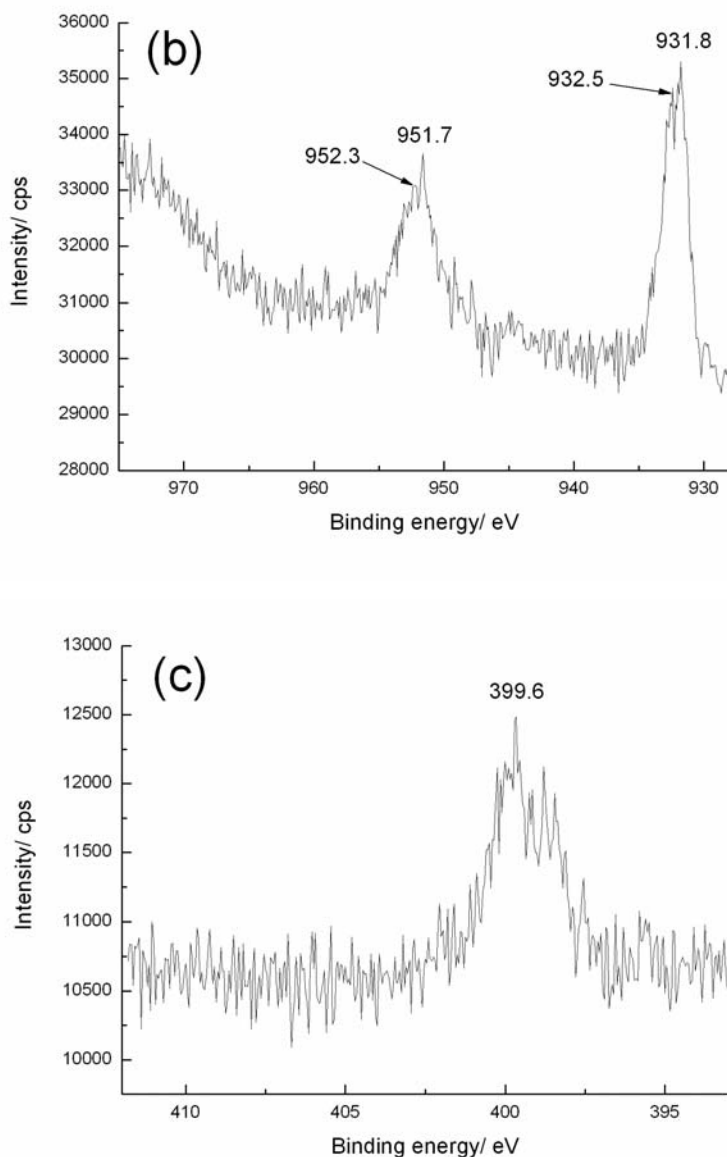


Fig. 4

### **.Figure Captions**

Fig. 1 Potentiostatic current transient curves for brass under thin electrolyte layer  
without and with DEAP at  $10^{-2}$  M

Fig. 2 SEM of specimen without (a) and with DEAP at  $10^{-2}$  M (b)

Fig. 3 The elements distribution of the protective film analyzed by EPMA  
BEI chart (a), distribution of Cu (b), distribution of Zn (c),  
distribution of N (d) and the single-line EPMA scan (e)

Fig. 4 XPS spectra of the protective film  
 $Zn_{2p}$  region (a),  $Cu_{2p}$  region (b) and  $N_{1s}$  region (c)