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Characterization of Bronzes by Abrasive Stripping Voltammetry and Thin Layer Chromatography*

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Corrosion potentials of five samples of bronzes having different compositions and the stripping peak potentials of their main components were determined by abrasive stripping voltammetry. Using thin-layer chromatography in combination with electrochemical dissolution of bronzes in the two electrode sampler, the ions of tin, copper, lead and nickel were detected as the products of electro-oxidation of bronzes. It is shown that the dissolution of tin is preferential at low potential differences between the electrodes in the sampler, while the electro-oxidation of copper is significant only at a potential difference higher than 8 V.

INTRODUCTION

Alloys are designed to optimize certain technical properties, such as mechanical strength, workability, wear and corrosion. If the metal objects involved are unique in nature (*e.g.,* statues, utility objects of different shapes and sizes in alloy), it is often necessary to sample with minor or even without destruction. There are only a few methods of chemical analysis known to satisfy these conditions. External beam proton induced X-ray emission spectrometry (PIXE)[1] and X-ray fluorescent (XRF) analysis[2] are nondestructive methods for *in situ* measurements, but they require sophisticated and expensive equipment. Micro-destructive methods are abrasive stripping voltammetry[3] and thin-layer chromatography after anodic sampling of metal.[4–8] All these methods give information about the chemical composition of the alloy surface, while the composition in the bulk of alloy cannot be determined without destruction. The advantage of nondestructive methods is the possibility to measure a larger number of surface samples taken at various positions on the object.

Abrasive stripping voltammetry and thin-layer chromatography after anodic sampling of metal are both based on anodic electro-oxidation of the alloy sample. Corrosion properties of alloys can be analyzed by measuring their electro-oxidation under potentiostatic,[9] voltammetric,[10] galvanostatic,[11,12] or pulse current[13] conditions. It was demonstrated that in some cases the preferential or selective anodic dissolution of the less noble metal in binary alloys should precede simultaneous dissolution, but generally the electro-dissolution mechanism depends on the method of measurement and the type of alloy.[9] In the

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* Dedicated to the memory of the late Professor Marko Branica.

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TABLE I. Composition of bronzes

	Mass fraction, w / %							
Alloy	Cu	Sn	Zn	Pb	Fe	Ni	Sb	Mn
CuSn3	79.07	20.21	0.09		0.06	0.007		
CuSn4	84.08	4.8	6.51	3.62	0.74	0.19	0.055	
CuSn5	86.03	11.62	0.1	0.03	0.06	2.14	0.01	0.01
CuSn6	87.46	12.54						
CuSn7	93.01	6.92	0.052		0.03	0.015		

galvanostatic mode, the dissolution changes gradually from preferential to simultaneous dissolution. The rate of dissolution of each component is proportional to its mole fraction at the alloy surface. At the beginning, selective corrosion of the components with relatively large rate constants results in a change of the composition of the alloy at the surface. Components corroding at relatively slow rates are enriched in the surface. The change of mole fractions of the components at the alloy surface leads to simultaneous dissolution under steady-state conditions. The total current density is determined mainly by the component with the largest product of the surface mole fraction and the rate constant. A well-known example of this de-alloying process is dezincification of brass caused by the preferential dissolution of zinc, which leaves a porous surface rich in copper.[12]

In anodic stripping voltammetry, the components of an ideal solid solution, intermediate phase and inter-metallic compounds are electro-dissolved simultaneously, but the dissolution of eutectic-type alloys is selective.[10] Selective dissolution can be used for voltammetric determination of the content of less noble components of binary alloys.[14] Complete chemical composition of alloys can be determined by using simultaneous galvanostatic dissolution of all components coupled to the atomic emission,[15] or absorption spectrometry.[16]

Experimental difficulties associated with the sample preparation for direct electrochemical analysis of alloys can be overcome by voltammetry of immobilized micro-particles.[3] This method is suitable for determination of the corrosion potential of metals[17] and for qualitative and quantitative analyses of alloys, amalgams[18–24] and ceramic glazes.[25,26] It is based on a mechanical transfer of traces of metals onto the surface of a paraffin-impregnated graphite electrode, and their subsequent electro-oxidation using anodic stripping voltammetry. The method is nondestructive because an extremely small quantity of material is abrasively transferred from the surface of the investigated alloy onto the electrode. Because of the minimized amount of sample, the resolution of stripping peaks is improved compared to the method in which the analyzed alloy itself is used as the working electrode.

In this communication, it is shown that the analysis of alloys can be improved by combining voltammetry of micro-crystals with electro-oxidation at constant potential, followed by the determination of dissolved ions using thin layer chromatography.[4–8,27]

EXPERIMENTAL

Experiments were performed with pure metals Sn, Cu, Pb, Zn and Ni in the form of thin foils, plates or nuggets, and with five samples of bronzes. The compositions of alloys are reported in Table I. Water was doubly distilled. The supporting electrolyte was 1.1 M HCl (Merck, analytical-grade).

Abrasive Stripping Voltammetry

Cyclic staircase voltammetry measurements were performed with a multimode polarograph μ-Autolab (Eco-Chemie, Utrecht) and a three-electrodes system consisting of a spectral-grade paraffin-impregnated graphite rod (PIGE, diameter 5 mm, length 50 mm) as the working electrode, a platinum wire counter electrode and an Ag | AgCl | 3 M KCl (Metrohm) reference electrode (E = 0.208 V *vs.* SHE). Before each measurement, the circular surface of the graphite rod was rinsed with distilled water, polished on a wet polishing cloth, rinsed again, dried with a fine-grade paper tissue and carefully polished on a dry, white paper sheet. The micro-crystals of metals and alloys were mechanically transferred to the electrode surface by rubbing the circular surface of the graphite rod on the surface of foils, plates or nuggets. Less than 1 mm of the graphite rod was immersed into the electrolyte in order to maximally restrict its contact with the solution to the working surface. PIGE contaminated with micro-crystals was connected to the potentiostat before it was immersed into the electrolyte. The potentiostat was activated 15 seconds before the electrode was fixed in the electrochemical cell. In this way, the PIGE was charged to the initial potential at the moment when its surface touched the electrolyte. Then, the stripping scan was initiated, with the rate of 100 mV/s in all measurements.

The electrolytes were degassed by an extra-pure nitrogen gas for 20 minutes prior to the measurement, and the nitrogen blanket was maintained thereafter.

Thin-layer Chromatography after Anodic Dissolution

Thin-layer experiments were performed on 100 × 200 mm microcrystalline cellulose pre-coated TLC plates of 0.1 mm layer thickness without fluorescent indicator (Merck, Darmstadt, Germany).

Chromatograms were developed with previous chamber saturation by the ascending technique to 7 cm distance. A mixture of methanol, hydrochloric acid (conc.) and water (vol. ratio, ψ(MeOH, HCl, H_2O) = 60 : 35 : 5) was chosen as the mobile phase for the development of chromatoplates.

The developed plates were dried in a stream of hot air and the ions were visualized by spraying with propanolic solution of quercetin (w = 0.1 %) and ethanolic solution of dimethylglyoxime (w = 1.0 %), and exposed to NH_3 vapour.[8]

Samples of alloys were prepared for TLC analysis and applied to TLC pre-coated layers by anodic sampling. Electrochemical dissolution of the sample was carried out with the help of a stabilized DC source built in the laboratory. The apparatus for anodic sampling comprised a pure graphite clip in a PVC holder with a nylon fiber tip connected to DC power supply. The graphite electrode clip was connected to the negative pole, and the tested metal plate to the positive pole of the DC power supply. Schematic presentation of the apparatus used was published elsewhere.[8] Hydrochloric acid solution was used as electrolyte, HCl(conc.) : H_2O = 1:10 (ψ). Hydrolysis of tin(II) ions is prevented in this medium. A new nylon fiber was used for each sampling. The sampling lasted 30 seconds and the transfer to chromatographic plates 20 seconds. To achieve optimum repeatability, sampling conditions were strictly time- and voltage-controlled.

The plates were developed and recorded. The chromatograms were captured under white light (reflectance) by means of the highly sensitive 3 x 1/2 inch CCD colour video camera HV-C20 (Hitachi, Denshi, Japan). Image acquisition, processing and archiving were controlled via the Video Store 2 version 2.30 documentation software running under Windows 95 (Camag, Muttenz, Switzerland).

RESULTS AND DISCUSSION

Abrasive Stripping Voltammetry

Cyclic voltamograms of Sn, Cu and Pb micro-particles immobilized on the PIGE surface, shown in Figure 1, are characterized by reversible redox reactions. Both anodic and cathodic peak potentials are lower (more negative) than the standard potentials of the corresponding metal electrodes. This is caused by the complexation of metal ions by chloride anions and by the rather small amount of metal particles on the electrode surface. The stripping peak of Sn particles appears at –0.422 V *vs.* Ag | AgCl | 3 M KCl (curve 1 in Figure 1a). It can be ascribed to the reaction: Sn + 4 Cl^- ⇔ $SnCl_4^{2-}$ + 2 e^-. The standard potential of the redox reaction Sn ↔ Sn^{2+} + 2 e^- is –0.344 V *vs.* Ag | AgCl | 3 M KCl. Curve 2 in Figure 1a shows that clean PIGE exhibits no activity in the investigated potential range. A small cathodic peak with the maximum at –0.643 V corresponds to the reduction of Sn^{2+} ions.

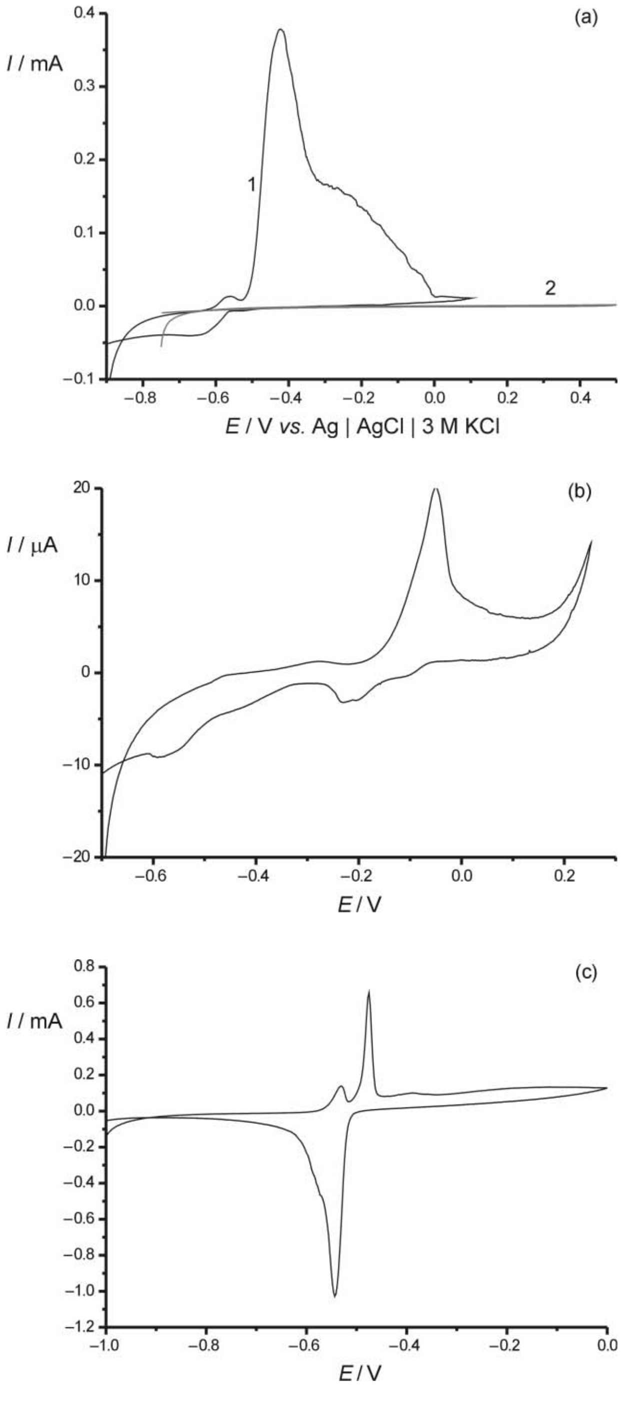

Figure 1. Cyclic staircase voltamograms of micro-crystals of Sn (a), Cu (b) and Pb (c) transferred from the foil to the surface of PIGE by abrasion. Curve 2 in (a): the response of pure PIGE. E_{start} = –0.9 V (a), –0.7 V (b) and –1 V (c); scan rate is 100 mV/s.

Electro-oxidations of copper and lead particles, with the stripping peaks at –0.051 V and –0.475 V, correspond to the reactions:[11] Cu + 3 Cl^- ↔ $CuCl_3^{2-}$ + e^-, and Pb + 4 Cl^- ↔ $PbCl_4^{2-}$ + 2 e^-, respectively. The potentials of main anodic and cathodic peaks are reported in Table II. Small anodic pre-peaks are probably caused by the adsorption of the complex ions.[12,18]

TABLE II. Anodic and cathodic stripping peak potentials and corrosion potentials of metals and bronzes[a]

Sample	E_{pa1} / V	E_{pa2} / V	E_{pc} / V	E_{corr} / V
Sn	–0.422		–0.643	–0.6
Cu		–0.051	–0.229	–0.43
Pb	–0.475		–0.544	
Zn		–0.041		
Ni		+0.113		–0.36
CuSn3	–0.239	–0.053	–0.241	–0.415
CuSn4	–0.189	–0.047	–0.328	–0.47
CuSn5	–0.175	–0.034	–0.209	–0.315
CuSn6	–0.178	–0.043	–0.217	–0.58
CuSn7	–0.231	–0.048	–0.221	–0.425

[a] All potentials are related to Ag | AgCl | 3 M KCl.

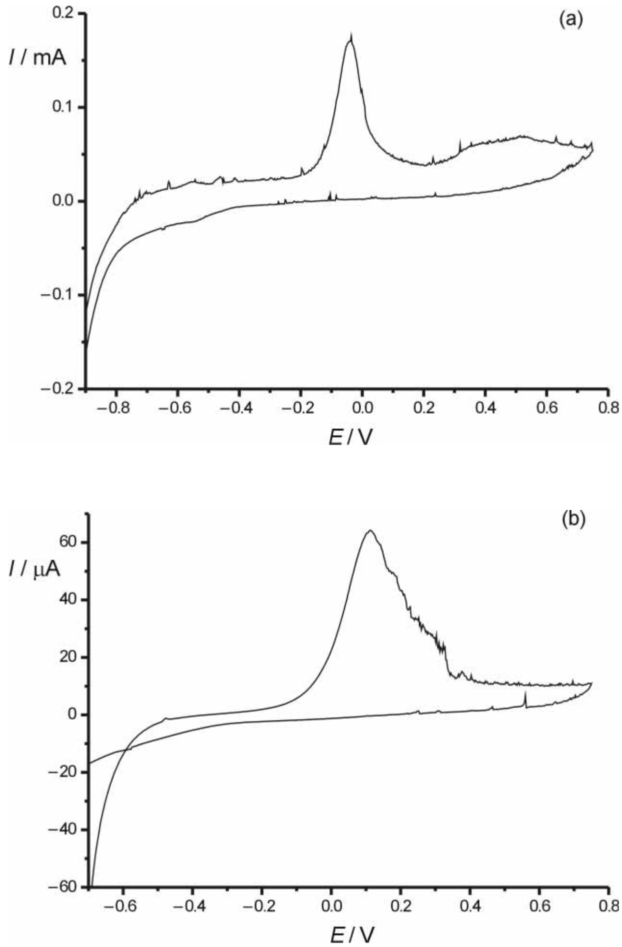

Figure 2. Cyclic voltamograms of Zn (a) and Ni (b) micro-crystals on PIGE.

Figure 2 shows voltammetric responses of totally irreversible electro-oxidations of micro-particles of Zn and Ni, with stripping peak potentials –0.041 V and +0.113 V, respectively. These values are much higher than the standard potentials of the redox couples Zn/Zn^{2+} (–0.971 V *vs*. Ag | AgCl | 3 M KCl) and Ni/Ni^{2+} (–0.444 V). Also, no reduction peaks appear in the cathodic branch of cyclic voltamograms.

Figure 3 shows the evaluation of voltammetric responses of Sn, Cu and Ni micro-crystals by means of Tafel plots. The values of corrosion potentials are listed in Table II.

Electro-oxidations of investigated bronzes are characterized by three stripping peaks, as can be seen in Figure 4. Their potentials are between –0.175 and –0.240 V (the first peak), between –0.034 and –0.053 V (the second peak) and between 0.35 and 0.5 V (the third peak). The values are reported in Table II for each alloy. Generally, the first peak is much smaller than the second and the third peaks, except in the case of CuSn5 (see Figure 4b). The first stripping peak is most probably caused by the oxidation of Sn, which is the main minor component of these alloys. These oxidations occur at higher potentials than the oxidation of pure Sn because of low Sn mole fractions in these alloys. The second peak corresponds to the oxidation of copper, as can be seen by comparison with Figure 1b. The third peak is most probably caused by oxidation of Cu^{+} to Cu^{2+} ions, as can be concluded from the increase of anodic current in this potential range, which is shown in Figure 1b. Also the main reduction peak in the cathodic branch of these cyclic voltamograms appears in the potential range between –0.209 and –0.241 V, which is in agreement with the reduction of copper ions at –0.229 V.

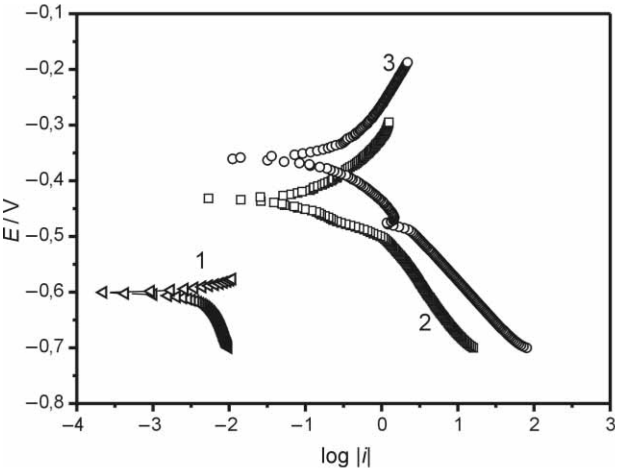

Figure 3. Semi-logarithmic presentation of polarization curves of Sn (1), Cu (2) and Ni (3) micro-particles on PIGE.

Figure 5 shows the determination of corrosion potentials of micro-particles of bronzes. The results, listed in Table II, are close to the values reported for copper and tin. The rather high corrosion potential of CuSn5 can be ascribed to the presence of nickel in this bronze.

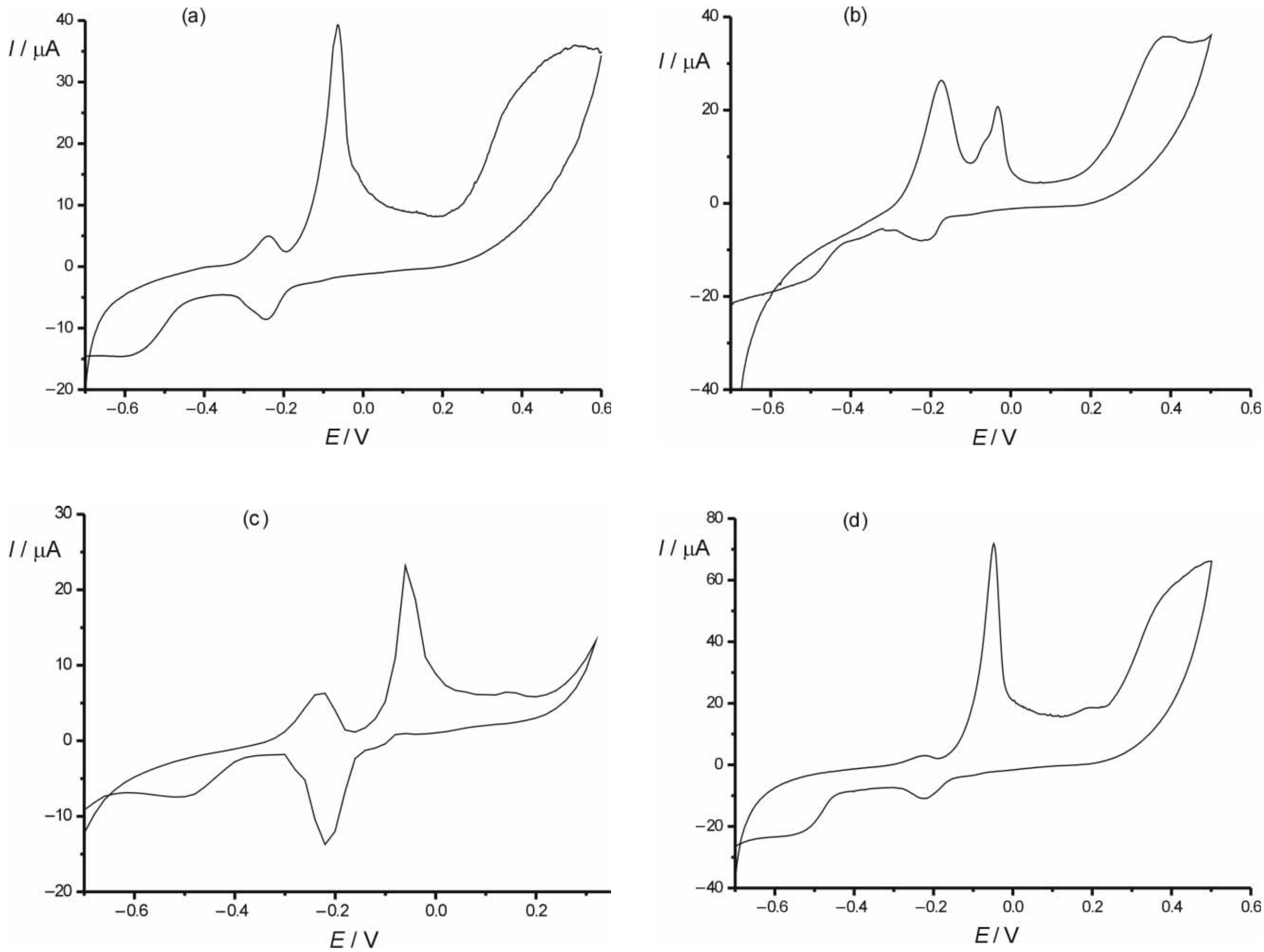

Figure 4. Cyclic voltamograms of abrasively transferred micro-particles of bronzes: CuSn3 (a), CuSn5 (b), CuSn6 (c) and CuSn7 (d).

Thin-layer Chromatography after Anodic Dissolution

The behavior of bronzes examined by TLC after anodic dissolution indicated the presence of copper, tin, lead and nickel. The intensity of chromatographic spots was measured by photometric scanning and expressed in arbitrary units (pixels). Figure 6 shows the dependence of the intensity of spots of Sn, Cu and Ni on the potential difference between the anode and cathode in the electrochemical sampler. The potential difference was changed from 3 V to 15 V, in increments of 0.5 V or 1 V. Measurements of pure metals (curve 1) are compared with the measurements of bronzes CuSn3 and CuSn5 (curve 2). The intensity of spots increases with the increasing potential difference, but this effect is more pronounced for copper than for the other two metals.

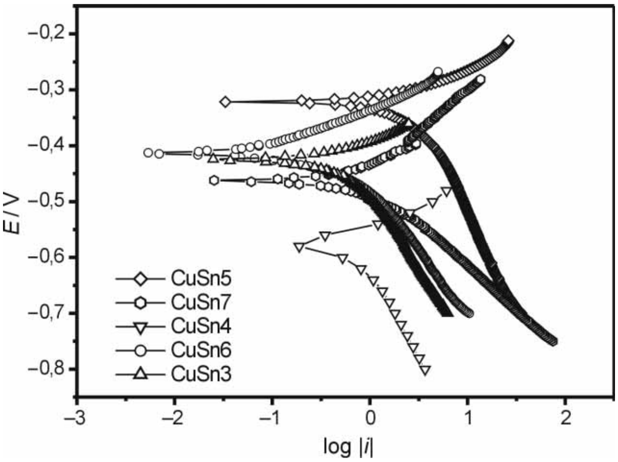

Figure 5. Polarization curves of micro-particles of bronzes.

Considering that the over-voltage of hydrogen evolution on graphite electrode is about –1 V *vs.* Ag | AgCl | 3 M KCl (see Figure 1c), the critical potential differences in the sampler for anodic dissolution of tin and copper are 0.6 V and 0.95 V, respectively. However, the working potential difference must be higher in order to compensate for the ohmic resistance within the sampler. It was shown previously[4] that the current in the sampler increases linearly with the increasing potential differ-

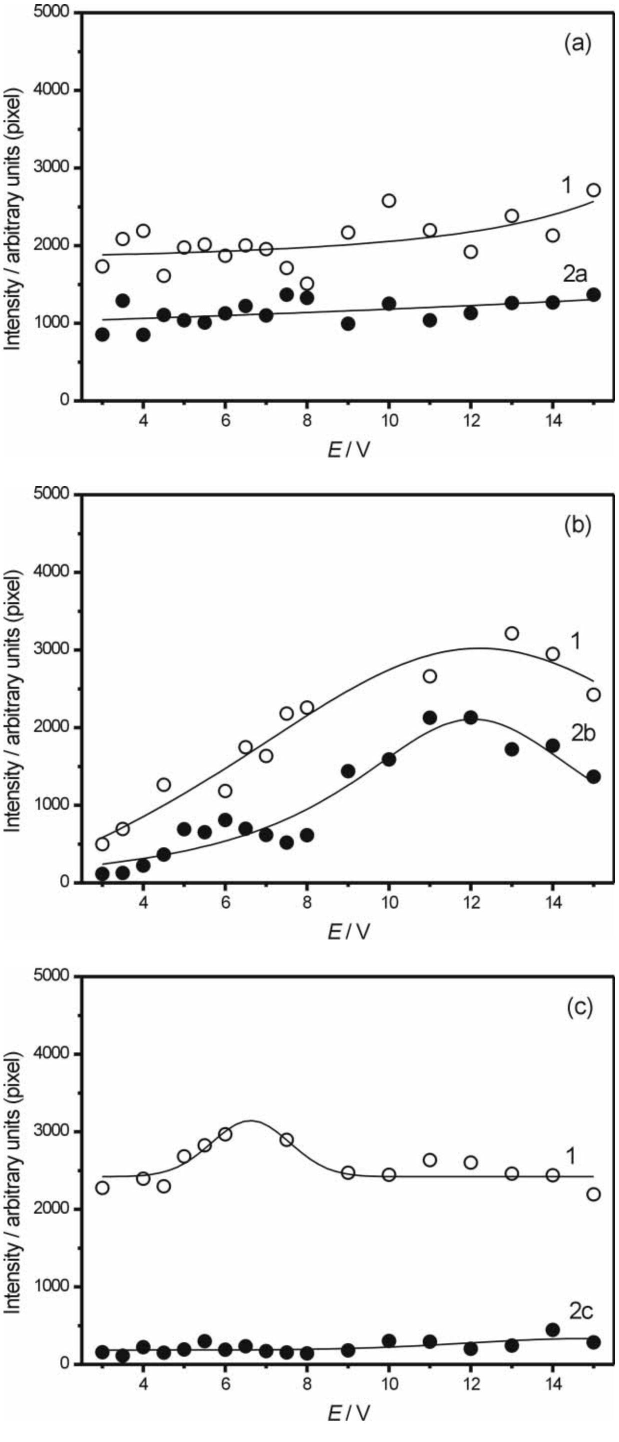

Figure 6. Dependence of the intensity of chromatographic spots of tin (a), copper (b) and nickel (c) on the potential difference in the sampler, for pure metals (1) and the bronzes (2) – CuSn3 (a) and (b), CuSn5 (c).

ence, if the difference is higher than 1 V. It seems that at high potential differences the current is carried not only by the dissolution of metal, or alloy, but also by the decomposition of the supporting electrolyte and water. The evolution of gases may create hydrodynamic conditions near the electrodes in the sampler.

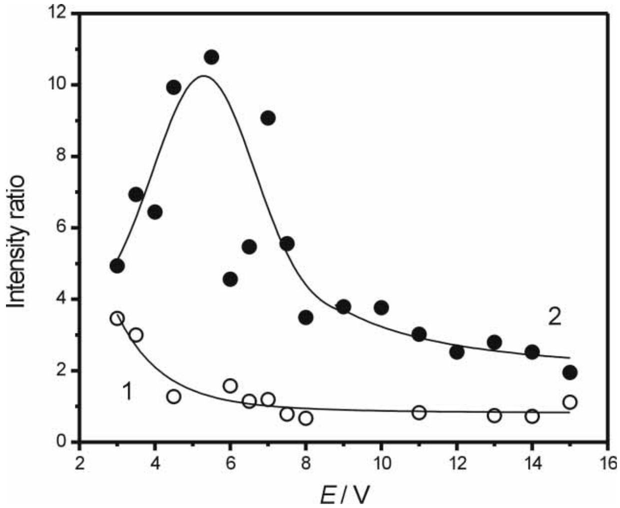

Figure 7. Dependence of the ratio of intensities of tin and copper spots on the potential difference in the sampler, for pure metals (1) and the bronze CuSn3 (2).

Curves 2 in Figures 6a and 6b show that the dissolution of tin from the bronze CuSn3 is significant at the lowest potential difference and increases only slightly at the highest potential difference, while the dissolution of copper, which is the main component of bronze, is significant only if the potential difference is higher than 8 V. The same effect was noticed with other bronzes, as well. Figure 7 shows the ratio of intensities of tin and copper spots as a function of the potential difference in the sampler. For the bronze CuSn3, the ratio is the highest if the potential difference is 5 V and decreases at higher differences. However, Figures 6 and 7 show that the dissolution of tin from the investigated bronzes is preferential, especially at low potential differences in the sampler.

These results confirm that the combination of abrasive stripping voltammetry with the thin-layer chromatography after anodic dissolution can improve qualitative analyses of alloys. The first method gives information about the potentials at which various oxidation processes occur during the electro-dissolution of alloys, while by the second method the ions released during the dissolution can be determined.

REFERENCES

1. T. Calligaro, J.-C. Dran, J. Salomon, and P. Walter, *Nucl. Instrum. Methods Phys. Res., Sect. B* **226** (2004) 29–35.
2. A. S. Serebryakov, E. L. Demchenko, V. I. Koudryashov, and A. D. Sokolov, *Nucl. Instrum. Methods Phys. Res., Sect. B* **213** (2004) 699–706.
3. F. Scholz and B. Meyer, in: A. J. Bard and I. Rubinstein (Eds.), *Electroanalytical Chemistry,* Vol. 20, Marcel Dekker, New York, 1998, pp. 1–86.
4. Z. Medanić, I. Eškinja, S. Turina, and F. Kovačiček, *Kem. Ind.* **38** (1989) 305–314.

5. Z. Medanić, V. Ivanković, and S. Turina, *Materialwiss. Werkstofftech.* **24** (1993) 195–197.
6. J. Živko-Babić, V. Ivanković, and J. Pandurić, *J. Chromatogr. B* **710** (1998) 247–253.
7. G. Schubert, V. Alar, J. Živko-Babić, and S. Turina, *J. Planar. Chromatogr. Mod. TLC* **11** (1998) 460–463.
8. A. J. M. Horvat, J. Živko-Babić, D. Ivanković, S. Babić, and M. Kaštelan-Macan, *J. Planar. Chromatogr. Mod. TLC* **14** (2001) 426–429.
9. K. E. Heusler, *Corros. Sci.* **39** (1997) 1177–1191.
10. R. Bertazzoli, M. Ballester Santos, and E. Bresciani, *Electrochim. Acta* **36** (1991) 1501–1503.
11. F. K. Crundwell, *Electrochim. Acta* **37** (1992) 2707–2714.
12. V. C. Machado, A. M. Schmidt, and D. S. Azambuja, *J. Braz. Chem. Soc.* **11** (2000) 387–392.
13. A. D. Davydov, *Electrochim. Acta* **43** (1998) 29–33.
14. N. Z. Blagojević, V. R. Kastratović, R. M. Zejnilović, and Ž. Blečić, *Fresenius J. Anal.Chem.* **371** (2001) 1023–1027.
15. I. G. Souza, H. Bergamin, F. J. Krug, J. A. Nobrega, P. V. Oliveira, B. F. Reis, and M. F. Gine, *Anal. Chim. Acta* **245** (1991) 211–216.
16. J. B. Borba da Silva, M. B. Oss Giacomelli, I. Goncalves de Souza, and A. J. Curtius, *Anal. Chim. Acta* **401** (1999) 307–315.
17. I. Žežula and M. Galova, *J. Solid State Electrochem.* **3** (1999) 231–233.
18. G. Cepria, O. Abadias, J. Perez-Arantegui, and J. R. Castillo, *Electroanalysis* **13** (2001) 477–483.
19. F. Scholz, L. Nitschke, and G. Henrion, *Fresenius Z. Anal. Chem.* **334** (1989) 56–58.
20. F. Scholz, L. Nitschke, and G. Henrion, *Electroanalysis* **2** (1990) 85–87.
21. F. Scholz, W. D. Muller, L. Nitschke, F. Rabi, L. Livanova, C. Fleischfresser, and C. Thierfelder, *Fresenius Z. Anal. Chem.* **338** (1990) 37–40.
22. Š. Komorsky-Lovrić and F. Scholz, *J. Electroanal. Chem.* **445** (1998) 81–87.
23. A. Minovič, I. Milošev, and Š. Komorsky-Lovrić, *Mater. Tehnol.* **34** (2000) 23–25
24. N. Souissi, L. Bousselmi, S. Khosrof, and E. Triki, *Mater. Corros.* 55 (2004) 284–291.
25. B. Meyer, B. Ziemer, and F. Scholz, *J. Electroanal. Chem.* 392 (1995) 79–83.
26. A. Domenech-Carbo, M. T. Domenech-Carbo, L. Osete-Cortina, J. V. Gimeno-Adelantado, F. Bosch-Reig, and R. Mateo-Castro, *Talanta* 56 (2002) 161–174.
27. A. Djeli, S. Turina, and F. Kovačiček, *Kem. Ind.* 33 (1984) 1–12.

SAŽETAK

Analiza bronce voltametrijom mikrokristala i tankoslojnom kromatografijom

Šebojka Komorsky-Lovrić, Alka J. M. Horvat i Danijela Ivanković

Određeni su korozijski potencijali pet uzoraka bronci različitoga sastava i potencijali oksidacije njihovih glavnih sastojaka. Kromatografskom je analizom dokazano da su produkti elektrokemijske oksidacije bronce ioni kositra, bakra, olova i nikla. Pokazano je da se kod malog napona u dvoelektrodnoj elektrokemijskoj ćeliji pretežito oksidira kositar, dok se bakar znatnije oksidira tek kod napona većih od 8 V.