

Determination of the zinc and cadmium contents in low-alloyed tin

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The method of anodic linear sweep voltammetry (ALSV) has been used to determine the content of Zn and Cd (up to 4% w/w) in eutectic type binary alloys with Sn. The alloy samples were prepared by casting. The effect of the type and the pH of the electrolyte, as well as of the sweep-rate on the dissolution of Zn and Cd from the alloy during an anodic potential-sweep was investigated. It was shown that ALSV is sensitive to low concentrations of both Zn and Cd in the investigated alloys, as well-defined peaks of the dissolution of the two metals were recorded before the massive dissolution of Sn commenced. Well-defined linear dependencies between the quantities of electricity under the dissolution peaks of Zn (Q_{Zn}) or Cd (Q_{Cd}) and the respective contents of the metals in the alloys were found. Intercepts at the abscissa were found in both investigated systems indicating the formation of solid solutions from which neither Zn nor Cd could be eluted. In both alloys, the smallest amount of the alloying component which could be detected was 0.25% (w/w). The application of the ALSV method has several advantages over other analytical methods: it is non-destructive as the dissolution involves only a very thin layer of the alloy; it requires simple and cheap instrumentation; it is fast and relatively sensitive. These make it suitable for routine analysis.

Key words: anodic linear potential sweep; Sn-Zn alloy; Sn-Cd alloy; analytical determination of Zn and Cd.

Electrochemical dissolution of alloys was the subject of scientific interest from the early days of electrochemistry. However, because of experimental difficulties and inadequate instrumentation at that time, it has so far found little use in analytical practice. Yet, electrochemical measurements offer significant information not only about the chemical composition but also about the structure of solids (metals, alloys). The applicability of anodic dissolution for the determination of the phase composition of alloys has been demonstrated in a number of papers.¹⁻⁵

In the large spectrum of electroanalytical methods,⁶ anodic dissolution has been used for qualitative and quantitative analysis of metals and alloys primarily by Sholz *et al.*⁷⁻¹⁹ The method used belongs to the category of "stripping analysis"

which affect only very thin layers of the analyzed samples so that it can be considered to be "non-destructive". Excellent results were achieved by abrasive stripping voltammetry. It consists of abrading minute quantities of a sample to be analyzed onto a parafine impregnated graphite electrode and analyzing it both qualitatively and quantitatively by recording anodic dissolution voltammograms.^{9–19} This method could be considered as indirect, as it requires transfer of material to another medium for analysis.

In recent years ALSV, as a direct method, has been used for the characterization of electrochemically deposited thin layers of alloys.^{20–28} This rendered data on both the chemical composition and the phase structure of alloys. It was shown that the essential requirement for the application of this method was a sufficient separation of the current responses to a changing potential, reflecting the dissolution of different metals or intermetallic phases. Hence, the deconvolution of the current peaks and the integration of the currents under them can be made as fully and as precisely as possible. This renders the quantities of electricity which are proportional to the quantities of the dissolved material.

In some simple cases of electrodeposited thin layers of eutectic type alloys, voltammograms with two widely separated peaks are obtainable. They sometimes also contain some intermediate peaks indicating the presence of minute quantities of some phase undetectable by any other method.²⁰ The results of analysis by this method are otherwise in agreement with the results of other (classical) methods of analysis of the same material.

The ALSV method is very easy to apply, requiring simple and cheap instruments. It is relatively sensitive to small amounts (1 percent and below) of substance in a sample. It requires simple preparation and is relatively fast (in the order of minutes) so that it is suitable for routine analysis. When thin layers are concerned, a disadvantage of this method is that it is destructive in the sense that the entire thin layer must be dissolved in order to determine the content of both components of a binary alloy.

The idea of using the method for the analysis of the bulk composition of some alloys was developed earlier.²⁹ It requires several conditions to be fulfilled:

- a) the alloy must be homogeneous in the sense that the composition and structure of the surface must be the same as that of the bulk;
- b) the dissolution of one component to a certain depth must occur at a potential sufficiently more negative than that of the dissolution of the more noble component in the bulk of the alloy so that the voltammogram renders a well-defined peak;
- c) the quantity of electricity under the peak must be proportional to the content (concentration) of that component in the alloy;
- d) the dissolution of that component should not cause cracks and notably increase the roughness of the surface.

With these requirements fulfilled, the method can be used for determining a low concentration of a less noble component in the bulk of a more noble metal.

The present work was stimulated by the fact that Sn has significant technical application³⁰ and, hence, a fast, cheap and non-destructive method for the routine analysis of the content of Zn and Cd in it is needed both in the production process and in its use. Sn builds eutectic type alloys with both Zn and Cd. Thus, Sn and Zn do not build any intermetallic compounds. Yet, Zn increases the brittleness of Sn, which hampers its technical application. On the other hand, as Sn deposits are resistant to corrosion in the presence of organic acids, they are used in food packing. Hence, the presence of poisonous Cd must be excluded. This gives importance to the analysis of the two components, which is the substance of this communication.

EXPERIMENTAL

Preparation of the alloy samples

The Sn-Zn and Sn-Cd alloys with a low content of Zn and Cd, respectively, were prepared by casting electrolytically obtained metals declared as 99.99%. The base metal was melted in a resistance furnace (CER, Čačak) in quantities of 500 g and the alloying element was added to the molten metal in quantities needed to make alloy samples containing between 0.5 and 4% of Zn or Cd. The samples were cut in 1 cm long parts. They had a copper wire soldered on top and then all the sides of a sample but one and the wire were insulated by an epoxy resin to prevent contact with the electrolyte. The naked side of the sample to be exposed to the electrolyte had a surface area of 1 cm².

The alloy surface was mechanically polished, first with wet polishing papers and then using a polishing cloth with Al₂O₃ polishing paste of grain size 0.3 and 0.05 μm. Immediately after polishing and before introduction into the electrochemical cell, the alloy samples were kept in an ultrasonic bath for 5 min to remove any traces of polishing material.

The content of the alloying element in each sample was determined by chemical analysis.

Solutions and preparation of experiments

Solutions for electrochemical dissolution of alloys were made of reagent grade chemicals and triply distilled water.

All experiments were carried out in a standard electrochemical cell at room temperature (close or equal to 25 °C). The electrolyte was purged in the cell free of oxygen by purified argon for 40 to 45 min.

A Pt foil of 1 cm² surface area was used as the counter electrode, while a saturated calomel electrode (SCE) served as the reference.

ALSV was performed with a potentiostat (Stonehart BC 1200), a universal programmer (PAR M-175) and an X-Y recorder (Houston Instruments 2000 R).

Procedure

After placing a sample in the cell and connecting it to the electronic circuit, its potential was set to a value some 50 mV more negative than that at which the alloying element starts dissolving. Then a potential sweep was started at a very low sweep rate (0.1 to 10 mV s⁻¹). After each sweep, which was ended at the potential of continuously increasing current (reflecting the start of dissolution of the base metal), the sample was taken out of the cell and the entire procedure of preparation (polishing and cleaning) was repeated before the next experiment. Characterization of each sample was repeated at least 10 times.

RESULTS

The system Sn-Zn

Four samples were prepared with varying Zn-content: 0.36 (1), 1.10 (2), 1.60 (3) and 3.60 (4)% (w/w).

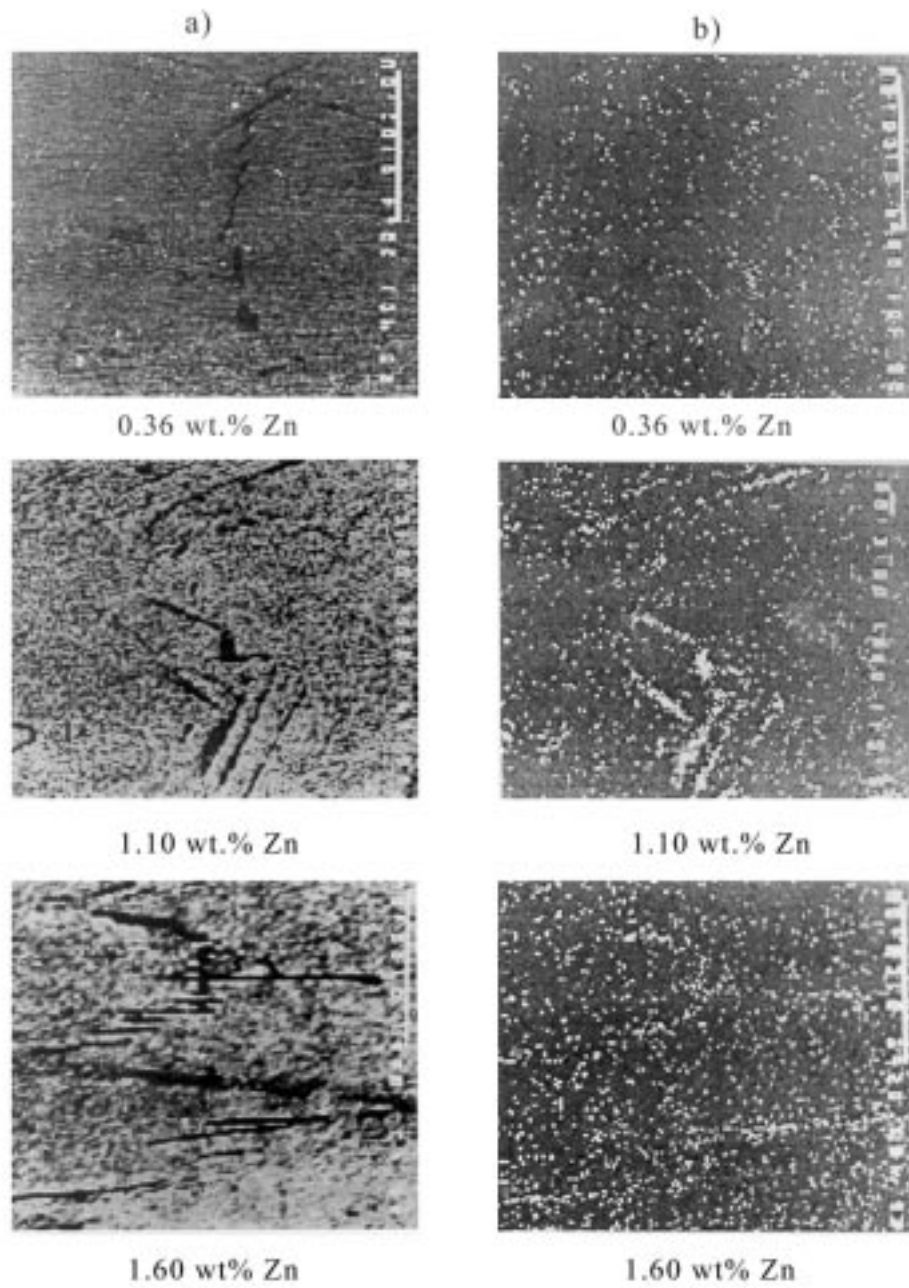


Fig. 1. SEM microanalysis of the distribution of Zn in the Sn-Zn alloys: a) microstructure; b) Zn distribution; bottom figures: after dissolution of Zn in the anodic sweep.

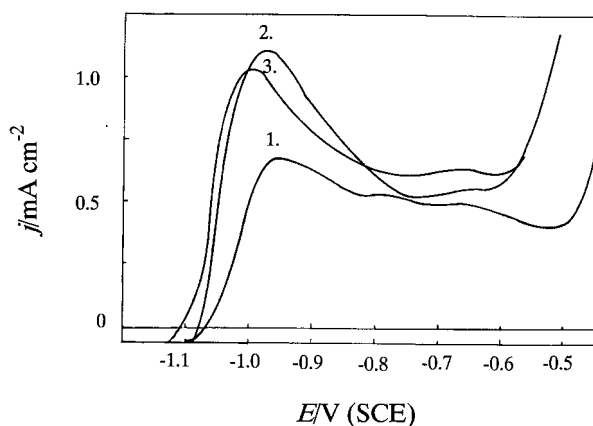


Fig. 2. Voltammograms of the dissolution of Zn from a Sn-Zn alloy with 0.36% (w/w) of Zn, at a sweep rate of 0.5 mV s^{-1} in different electrolytes. 1) 1 M NH_4Cl , pH 4.47; 2) 3 M NH_4Cl , pH 4.63; 3) 1 M KCl , pH 2.6.

The qualitative metallographic investigation by SEM, shown in Fig. 1, revealed the presence of some coarse crystals in the bulk of the alloy. It can be seen that the Zn content is higher in the coarse crystals than in the bulk in which it appears homogeneously dispersed.

ALSV was tested in three different electrolytes, as seen in Fig. 2. The best result in terms of the expression of the Zn peak was obtained in 3M NH_4Cl . Hence, all further experiments were carried out in this electrolyte with a variation of sweep rate from 0.1 and 10 mV s^{-1} and of pH between 1.5 and 4.5

It can be seen that the dissolution peak at -0.95 V is well separated from the continuous increase of current appearing at about -0.63 V .

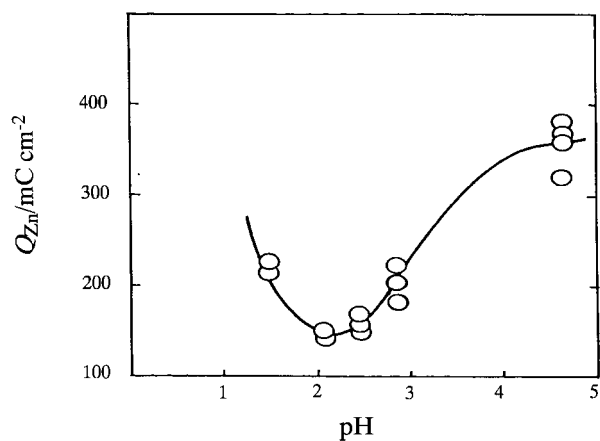


Fig. 3. The quantity of electricity, Q_{Zn} , obtained by integration of the dissolution peak of Zn from a Sn-Zn alloy with 0.36% (w/w) of Zn in 3 M NH_4Cl , at a sweep-rate of 0.5 mV s^{-1} , as a function of pH.

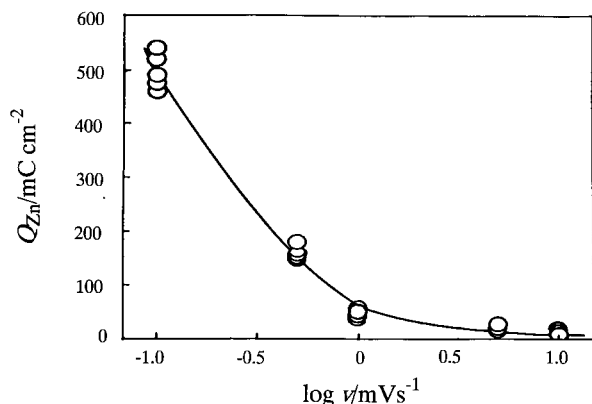


Fig. 4. Sweep-rate dependence of Q_{Zn} obtained in 3 M NH_4Cl of pH 2.

Figure 3 demonstrates the effect of pH. It can be seen that the quantity of electricity obtained by integration exhibits a minimum at a pH around 2, while a fair amount of electricity is recorded at pH 4.5.

The sweep rate had a significant influence on the amount of electricity under the peak before massive dissolution, as shown in Fig. 4. Any sweep rate above 1 mV s^{-1} rendered an amount of electricity under the Zn peak too small to be used for Zn content analysis with satisfactory precision. Although a sweep rate of 0.1 mV s^{-1} gives the most favourable result in terms of Q and, hence, attainable precision, it is too low for practical use as it requires about 1 h for one whole sweep. Hence, a sweep rate of 0.5 mV s^{-1} was used in further experiments.

Typical voltammograms obtained with the alloys of different Zn content are shown in Fig. 5. Although Zn dissolution peaks are well expressed, the voltammograms exhibit long tails as well, before the start of massive dissolution, suggesting the presence of another peak.

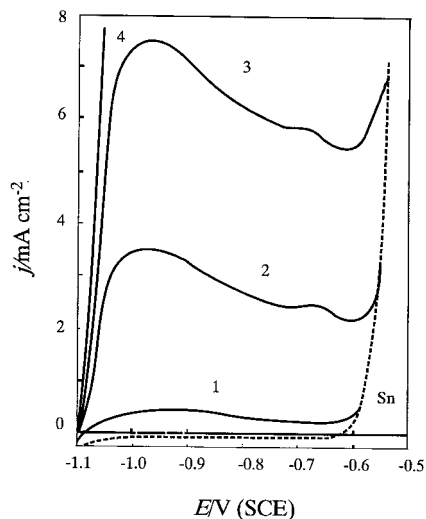


Fig. 5. Voltammograms of the dissolution of Zn from Sn-Zn alloys of different Zn content in 3 M NH_4Cl , pH 4.6 at a sweep rate of 0.5 mV s^{-1} : 1) 0.36; 2) 1.10; 3) 1.60; 4) 3.40% (w/w) Zn.

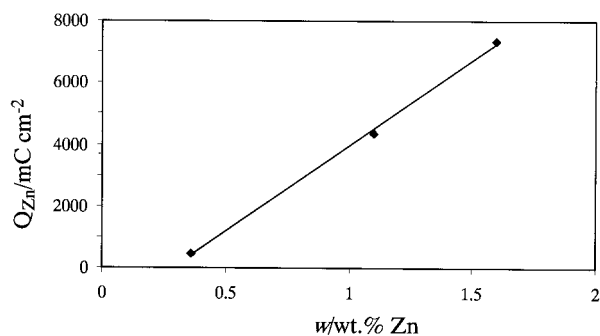


Fig. 6. Average Q_{Zn} as a function of Zn content in Sn-Zn alloys. 3 M NH_4Cl , pH 4.6; sweep-rate 0.5 mV s^{-1} .

Hence, integration must involve the current up to the potential of continuous current rise. However, as that rise, reflecting dissolution of Sn, is very sharp, deconvolution of the Zn and Sn dissolution currents can be done with fair precision.

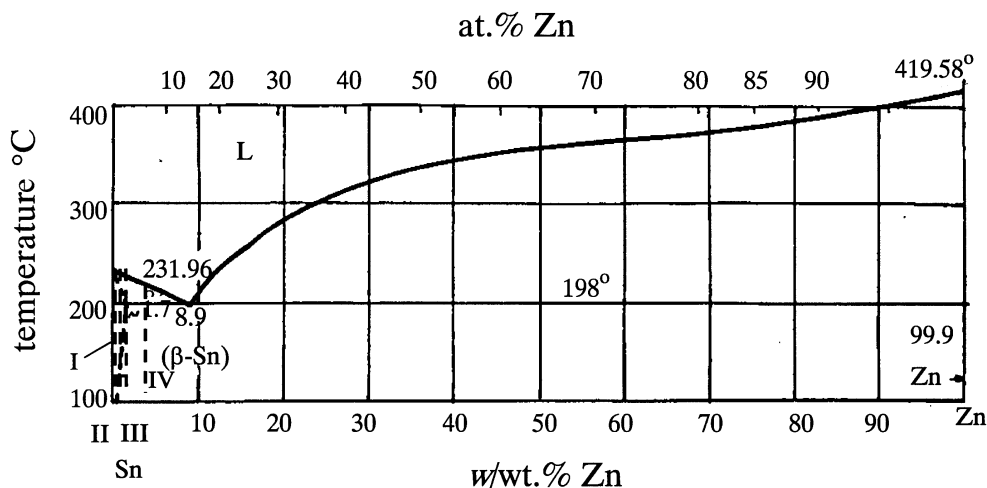


Fig. 7. Phase diagram of Sn-Zn alloys.

The dependence of the quantity of electricity under the Zn peak on Zn content is given in Fig. 6. It is seen to exhibit fair linearity, somewhat deviating at the highest Zn content. The straight line, however, does not pass through the origin, but has an intercept with the abscissa at about 0.3% (w/w) of Zn. Statistical evaluation of the results was carried out and the results are presented in Table I.

TABLE I. Statistical evaluation of the data on the charge obtained upon anodic dissolution of samples of Sn-Zn alloys of different Zn content at a sweep rate of 0.5 mV s^{-1}

| %Zn(w/w) | <i>n</i> | $(Q_{\text{Zn}})_{\text{av}}/\text{mC cm}^{-2}$ | <i>RSD</i> /% |
|----------|----------|---|---------------|
| 0.36 | 10 | 1.8×10^2 | 1.0 |
| 1.10 | 10 | 3.7×10^3 | 0.4 |
| 1.60 | 10 | 6.1×10^3 | 4.6 |

n—Number of samples tested; $(Q_{\text{Zn}})_{\text{av}}$ —average charge under the dissolution peak; *RSD*—relative standard deviation

The system Sn-Cd

The alloy Sn-Cd at low content of Cd renders similar voltammograms as the alloy Sn-Zn. The alloy samples used in the analysis had following Cd contents: 0.66 (1); 0.87 (2); 1.27 (3) and 2.24 (4) % (w/w).

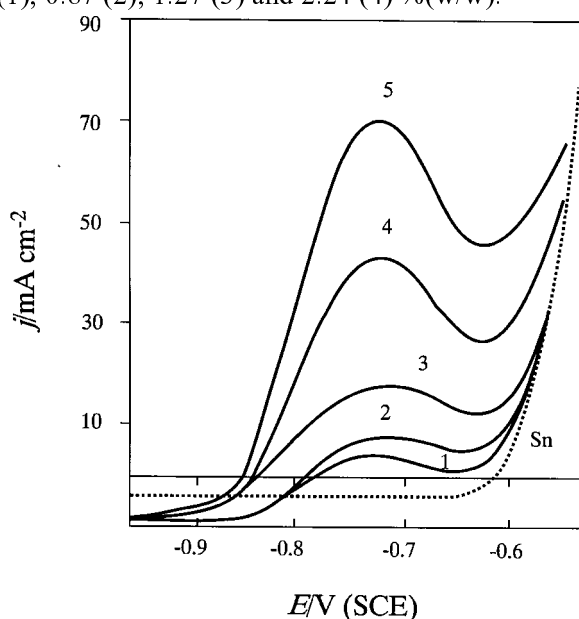


Fig. 8. Voltammograms of the dissolution of Sn-Cd alloys of different Cd content in 3 M NH_4Cl , pH 2.5 at a sweep rate of 0.5 mV s^{-1} : 1) 0.66; 2) 0.88; 3) 1.28; 4) 1.43; 5) 2.24% (w/w) of Cd.

Figure 8 shows typical voltammograms of the dissolution of a Sn-Cd alloy. They are seen to exhibit a single peak at significantly more positive potential (-0.73 V) than in the case of the Sn-Zn alloy, yet sufficiently divorced from the current rise due to massive dissolution, as to provide satisfactory deconvolution and integration.

The pH dependence of the quantity of electricity under the peak Q_{Cd} (Fig. 9) exhibits a minimum at similar pH value as in the previous case. The sweep-rate dependence of Q_{Cd} is shown in Fig. 10. Here, 0.5 mV s^{-1} was also taken as the optimum for further use. The dependencies of Q_{Cd} on the Cd content of the alloy at different sweep-rates and different pH values are seen in Fig. 11. It can be seen that linear relationships are obtained in all cases. They are also seen to extrapolate to about 0.15–0.25% (w/w) of Cd at the abscissa.

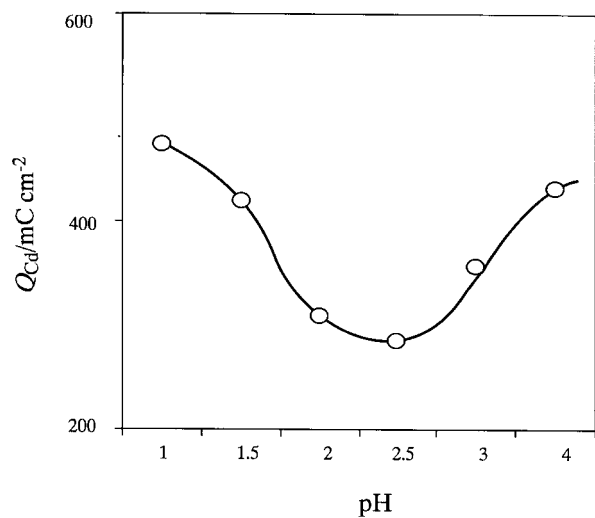


Fig. 9. pH dependence of the quantity of electricity, Q_{Cd} , obtained by integration of the Cd peaks in the potential-sweep dissolution of Sn-Cd alloys, 3 M NH_4Cl , sweep rate $0.5\ mV\ s^{-1}$.

Statistics was also worked out for this system and the result is shown in Table II.

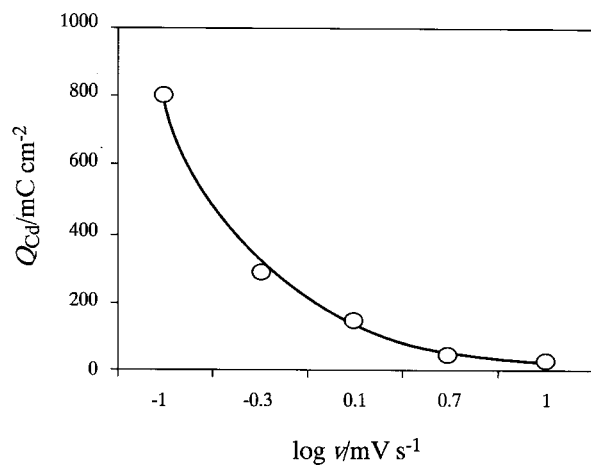


Fig. 10. Q_{Cd} of a Sn-Cd alloy with 1.43% (w/w) of Cd as a function of sweep rate in 3 M NH_4Cl of pH 2.5.

TABLE II. Statistical evaluation of the data on the charge obtained upon anodic dissolution of samples of Sn-Cd alloys of different Cd content at a sweep rate of 0.5 mV s^{-1}

| %Cd (w/w) | <i>n</i> | $(Q_{\text{Cd}})_{\text{av}}/\text{mC cm}^{-2}$ | RSD/% |
|-----------|----------|---|-------|
| 0.66 | 10 | 2.1×10^2 | 2.1 |
| 0.87 | 10 | 1.6×10^2 | 4.4 |
| 1.27 | 10 | 2.3×10^2 | 1.3 |
| 1.43 | 10 | 2.6×10^2 | 2.3 |
| 2.24 | 10 | 4.1×10^2 | 2.1 |

n—Number of samples tested; $(Q_{\text{Cd}})_{\text{av}}$ —average charge under the dissolution peak; RSD—relative standard deviation

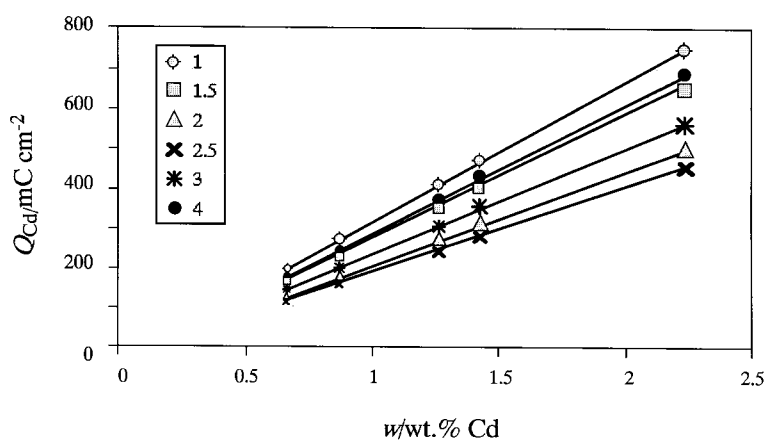
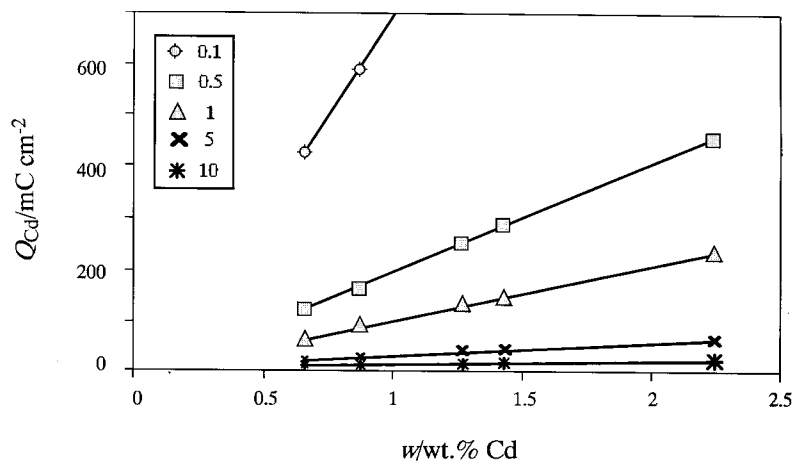


Fig. 11. Q_{Cd} as a function of Cd content in Sn-Cd alloys dissolved in 3 M NH₄Cl, a) at different sweep rates (at pH 2.5) and b) at different pH (at a sweep rate of 0.5 mV s^{-1}).

DISCUSSION

The phase diagram of the Sn-Zn alloy is shown in Fig. 7. It indicates that the two metals are immiscible in the solid state, forming a eutectic with 8.9% (w/w) of Zn. The SEM microanalysis (Fig. 1) shows, however, more Zn in the coarse crystals, which are supposed to be formed in the early stage of solidification, than in the bulk solidifying at the temperature of the eutectic. This could be ascribed to the crystallization kinetics, whereby, contrary to the equilibrium situation, even at very low Zn contents a Zn (or a Zn-rich phase) crystallizes first in the bulk of the liquid Sn during the cooling process. Indeed, as seen in Fig. 1 (bottom), the micrographs obtained after the sample had been submitted to ALSV, show that the coarse crystals had vanished, while still some Zn remained homogeneously dispersed in the bulk of the alloy. Hence, it appears that the Sn-Zn system renders a highly non-equilibrium alloy on casting. It could be concluded that it is the coarse crystals which dissolve first in the anodic process and are responsible for the first current peak. The second current peak or the "tail" of the voltammogram is likely to represent dissolution of Zn from the bulk of the alloy, close to the potential of the bulk dissolution itself, where it is likely to be in small grains characteristic of eutectics in the sea of solid Sn.

An aqueous solution of NH_4Cl of high concentration was taken as the electrolyte for the anodic dissolution because of polarographic data⁶ as well as data of Pohelnikov *et. al.*³²

The pH dependence of the quantity of electricity due to Zn dissolution, Q_{Zn} , obtained during the sweep, which is shown in Fig. 3, could be explained as follows:

Zinc ions in aqueous chloride solutions forms complexes with both Cl^- and OH^- ions. It appears that the OH^- complexes are formed faster, even at very low OH^- ions concentration as is the case at pH 4 to 5, than the Cl^- complexes. Hence, the amount of Zn dissolved at higher pH during the time period of the sweep is larger than that at lower pH values.

The crucial result from the point of view of analytical application is the Q_{Zn} dependence on the Zn content of the alloy, shown in Fig. 6. The intercept at about 0.3% (w/w) of Zn indicates that, contrary to the phase diagram, some Zn remains in the solid solution from which it is dissolved together with Sn.

Similar results were obtained with the Sn-Cd alloys. A similar relative standard deviations is seen in both cases. Statistical evaluations, presented in Tables I and II, indicate that the method offers precision acceptable in routine analysis.

An interesting issue is the depth of penetration of dissolution into the bulk of the alloy, *i.e.*, the thickness of the layer dissolved in the process. It is possible to calculate this on the basis of the following reasoning: Assuming that dissolution is even over the entire surface and that the mass of the dissolved metal, g_{M} , is related to the amount of electricity Q_{M} according to

$$g_{\text{M}} = \frac{Q_{\text{M}}M}{2F} \quad (1)$$

where M is the molar mass of the dissolved metal. With the content of the metal w_M homogeneously distributed in the bulk of the alloy, the volume dissolved per cm^2 , V , which is equal to the thickness of the dissolved layer, d , should be

$$V = d = \frac{g}{w\rho} = \frac{MQ}{2F\rho w} \quad (2)$$

where ρ is the density of the alloy. For a changing content of the alloying metal

$$d = \frac{M}{2F\rho} \frac{dQ}{dw} \quad (3)$$

where dQ/dw is the slope of the dependencies shown in Figs. 6 and 11. Figure 11 shows that d depends on both the sweep rate and pH. This is due to the fact that these parameters affect the Q_M by affecting the time the dissolution lasts and the rate of dissolution.

Taking as typical, *e.g.*, a sweep rate of 0.5 mV s^{-1} and a pH of 4.6, for the case of the Sn-Zn alloy, with $dQ/dw = 0.535 \text{ C cm}^{-2}/\%$, one obtains d of $2.5 \times 10^{-5} \text{ cm}$ dissolved during the 1000 s of the sweep duration.

In the case of Sn-Cd alloy one arrives at $d = 1.6 \times 10^{-5} \text{ cm}$.

On the bases of the above calculation, it could be concluded that only a very thin layer, of the order of 100 nanometers, is dissolved during the analysis. Hence, the method can be considered as non-destructive.

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ИЗВОД

ОДРЕЂИВАЊЕ САДРЖАЈА ЦИНКА И КАДМИЈУМА У НИСКО-ЛЕГИРАНОМ КАЛАЈУ

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Метода анодне линеарне промјене потенцијала (АЛПП) коришћена је за одређивање садржаја цинка и кадмијума (до 4 теж. %) у еутектичком типу двокомпонентних легура калаја. Узорци легура су припремани металуршким поступком. Испитиван је утицај врсте и рН електролита као и утицај брзине промјене потенцијала на растварање Zn и Cd из поменутих легура примјеном методе АЛПП. Показано је да је АЛПП метода осјетљива на ниске концентрације Zn и Cd у испитиваним легурама, као и да су забиљежени добро дефинисани струјни врхови растварања Zn и Cd прије него што почне растварање Sn. Нађено је да се добијају добро дефинисане линеарне зависности између количине наелектрисања испод струјних врхова растварања Zn (Q_{Zn}) одн. Cd (Q_{Cd}) и садржаја метала у легурама. У оба испитивана система нађен је одсјечак на апсциси, што указује на формирање чврстих раствора из којих се ни Zn ни Cd не могу растворити

примјеном методе АЛПП. У оба испитивана система најмања количина легирајућег елемента (Zn или Cd) која се могла детектовати износила је 0,25 теж. %. Примјена АЛПП методе има неколико предности у односу на друге аналитичке методе: метода је недеструктивна пошто се раствара само веома танак слој легуре; за њену примјену потребна је једноставна и јефтина инструментација; брза је и релативно осјетљива. Ове карактеристике је чине подесном за рутинске анализе.

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