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Research Paper**Anodic Behaviors of Metals in the Nonaqueous Sulfamic Acid-Dimethylsulfoxide System**

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Anodic dissolution and polishing of eleven metals (Ag, Bi, Cd, Co, Mn, Mo, Sn, Pb, Ni, Ti and Ta) in the nonaqueous sulfamic acid dimethylsulfoxide solution (DMSO) were investigated and results were compared with that in the nonaqueous sulfamic acid-formamide solution.

To measure the electrode potential in the nonaqueous DMSO solution, a reversible reference electrode must be selected first.

It was found in the preliminary experiment that Ag/AgClO₄ in DMSO electrode was a non-polarizable and stable reference electrode in this system. Furthermore its recovery characteristics was found to be less than 5 msec. after the current interruption.

Ag/AgClO₄ in DMSO electrode was therefore used as reference electrode. From the anodic polarization behavior, metals can be classified into three groups: The 1st is Ti and Ta. They showed very high overvoltage, forming eventually anodic films.

The 2nd is Mo, which showed relatively high overvoltage, forming viscous layer on the surface. The 3rd is Ag, Cd, Co, Bi, Sn, Mn, Pb and Ni. They showed relatively low overvoltage and were anodically brightened, except for Pb and Ni.

The current efficiency of the anodic dissolution was found to be ca. 100% for Ag, Bi, Cd, Sn and Pb and very low for Ni.

Taking into consideration of electropolishing in the formamide solution, conditions and processes of electropolishing in the DMSO solution are discussed.

1 Introduction

Anodic behaviors of common metals in aqueous solutions were widely investigated, however very seldom in nonaqueous solutions.

Vecchia et al.¹⁾ investigated the anodic behavior of metals in the aqueous sulfamic acid solutions, whereas Tajima et al.²⁾ reported the possibility of electropolishing of zinc, cadmium and molybdenum in the aqueous sulfamic acid solution and also reported that the local brightening of the surface was observed on copper, tin and lead.

Recently, Menzies et al.³⁾ investigated the anodic behavior of metals in 1.0M sulfamic acid in for-

amide solutions using a potentiostatic techniques, where Cu, Sn, Pb, Zn, Cd, Ag, Ti, U, Mo and W were electropolished. Recently, the nonaqueous solvent, dimethylsulfoxide became very interested in the field of electrochemistry, since this solvent has relatively large dielectric constant (46.6) and dipole moment (4.3 Debye). The lack of the investigations concerning the electrochemical behavior of metals in the sulfamic acid-dimethylsulfoxide system suggested that the studies on the anodic and cathodic polarization behavior of metals would be very tentative subject.

In the present experiment, anodic behavior of eleven metals were observed in the nonaqueous sulfamic acid-dimethylsulfoxide solution and the following results

were obtained:

1. electropolished or brightened Mn, Ag, Cd, Sn, Mo, Bi, Co, Ni
2. oxide film formation Ti, Ta
3. active dissolution Pb

2 Experimentals

Dimethylsulfoxide of 99.9% purity was refluxed for two hours in contact with calcium hydride and distilled at a reduced pressure of approximately 1 mmHg. The middle distillate was again distilled at the same pressure and the final distillate gave the specific conductivity of $5 \times 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$.

The guaranteed reagent of sulfamic acid, which is non-hygroscopic and kept in a vacuum desiccator, was used for the experiment without further purifications.

All solutions had a sulfamic acid concentration of 1.0M/l and the guaranteed reagent grade of silver perchlorate was heated to 50°C in the nitrogen atmosphere and used as a electrolyte for the reference electrode.

The metals (Cd, Sn, Pb, Ag, Bi, Mn, Co, Ni, Mo, Ti, Ta) used as the working electrode were prepared as follows:

1. abraded with the 600 grade SiC paper
2. etched in 10% HNO₃, except Mo, Ti and Ta
3. washed with guaranteed acetone, and
4. dried in a stream of warm nitrogen gas.

Reference electrode was composed of Ag/Ag⁺ in 0.05M AgClO₄ in dimethylsulfoxide. In order to control the reproducibility, four silver electrodes having the geometric surface area of 20 cm² were arepared and immersed in 0.05M AgClO₄ solution.

It was found that the fluctuation of the potential of each electrode was negligible. Since silver perchlorate is decomposed by light and metallic silver is sensitive to atmospheric oxygen, the brown glass cell was used and sealed with silicone plug.

The cell for the polarization measurement is shown in Fig. 1.

The capacity of the cell is 200 ml, and the working electrode and Pt-counter electrode have the geometric surface area of 1 cm² and 8 cm², respectively. The reference electrode is related to the cell through two separate compartments (S₁ and S₂) and two bridges (sat. NaClO₄ and 1.0M NH₂SO₃H).

Polarization curves were measured with potentiometer (Cambridge and paul Instrument CO., Ltd.) and galvanostat (Metronics 691 A).

The stationary electrode potential was measured after the constant current was passed for five minutes.

To confirm the reversibility of the reference electrode, Ag/Ag⁺ in 0.05M AgClO₄-dimethylsulfoxide solution

A: Argon inlet and outlet, S: Solution inlet, W: Working electrode, C: Pt counter electrode, L: Luggin capillary, E: Silicone rubber, D: Sintered disk, B: Salt bridge (satd. NaClO₄), S₁: 1.0M NH₂SO₃H, S₂: 0.05M AgClO₄, R: Reference electrode Ag/Ag⁺ in 0.05M AgClO₄, dimethylsulfoxide

Fig. 1 Cell arrangement for galvanostatic studies

was polarized in the same cell without compartments, and the relation between potential and current density was measured in the vicinity of its equilibrium potential.

3 Results and Discussion

3.1 Ag/Ag⁺ reference electrode

It must be checked if the reference electrode used is fit for the measurements in nonaqueous dimethylsulfoxide solution. For this purpose, four identical Ag-electrodes were prepared and the potential difference between each electrode was checked for ten days and after the polarization measurement of metals. The reversibility and the recovery velocity were also examined.

It was found that the maximum potential difference between each reference electrode was only 4.7 mV in ten days after preparation. Another point that must be checked is the recovery of the reference electrode after polarization. Ag-electrode prepared in the same way as the reference electrode was polarized to ± 50 mV in 0.05M AgClO₄ solution and then the decay of the potential was followed by a potentiometer and an oscilloscope after the current was cut off.

The result showed that the overvoltage was less than 0.2 mV after 10 seconds of current interruption and the potential recovered the original value within 5 milliseconds. Ag/Ag⁺ electrode is therefore usable for the measurements of the electrode potential as reference electrode in the compensation circuit.

3.2 Polarization behavior of Ag-electrode in 0.05M AgClO₄, dimethylsulfoxide solution

Anodic and cathodic polarization curves of silver

Fig. 2 Relationship between current density and overvoltage of the silver electrode in 0.05 M AgClO_4 DMSO solution at 25°C

plate ($1.0 \times 1.0 \text{ cm}^2$) in 0.05 M AgClO_4 dimethylsulfoxide solution was shown in Fig. 2, in which a linear relationship between overpotential and current density was observed in the potential range from -15 to +5 mV.

Since the current density regulated by the charge transfer reaction is expressed by the following equation:

$$i = i_0 \{ \exp(\alpha n F \eta / RT) - \exp[-(1-\alpha) n F \eta / RT] \} \quad (1)$$

and when η is small enough, the expansion of the eq. 1 gives a linear relationship between current density and overpotential.

$$i = i_0 \frac{nF}{RT} \eta \quad (2)$$

The exchange current density calculated from the slope was $6.3 \times 10^{-6} \text{ A/cm}^2$. Charge transfer reaction is

This value for the electrodeposition of silver from the simple nonaqueous dimethylsulfoxide solution and vice versa seems to be reasonable compared with the other simple aqueous systems; 10^{-8} A/cm^2 from 1.25 M FeSO_4 , 10^{-10} A/cm^2 from 1.0 M $\text{Cu}(\text{NO}_3)_2$, $2 \times 10^{-5} \text{ A/cm}^2$ from 1.0 M CuSO_4 , $2 \times 10^{-5} \text{ A/cm}^2$ from 1.0 M ZnSO_4 and $2 \times 10^{-9} \text{ A/cm}^2$ from 1.0 M NiSO_4 ^{5), 6)}.

3.3 Anodic polarization behavior of metals in 1.0 M $\text{NH}_4\text{SO}_3\text{H}$ dimethylsulfoxide solution

Anodic polarization curves of various metals measured by the galvanostatic method was shown in Fig. 3 and 4. The curves can conveniently be classified into three groups according to the shape of the curves and the

Fig. 3 Relationship between overpotential and anodic current density in 1.0 M sulfamic acid at 25°C

Fig. 4 Relationship between overpotential and anodic current density in 1.0 M sulfamic acid at 25°C

order of the overvoltage.

group 1; Ti and Ta

These metals have a large overvoltage and the

polarization curves showed the steep increment of the overvoltage with increasing current density. There were the limiting current density of about 2×10^{-4} for Ti and 4×10^{-4} A/cm² for Ta. In the case of Ti, gas evolution and arcing were observed at 5 mA/cm² and 10 mA/cm², respectively, whereas in the case of Ta, interference colored film appeared at 5 mA/cm² and gas evolved at 30 mA/cm².

The formation of the solid oxide film is obviously the cause of high overvoltage.

group 2; Mo

This metal has also a relatively high overvoltage. During electrolysis brown viscous layer streamed down from the anode surface and electropolishing occurred (Photo. 1).

group 3; Ag, Co, Pb, Cd, Sn, Bi, Mn and Ni

These metals which are the typical metals to be electropolished in aqueous solutions were also electropolished in nonaqueous solution except for Pb and Ni*. Polarization curves showed generally low overvoltage in the range of low current density, while in the range of high current density ($>10^{-3}$ A/cm²), over-

Photo. 1
Fused-like surface of Mo after electropolished at 50 mA/cm² and for 100 minutes, $\times 280$

Photo. 2
Structure of Co electropolished at 6 mA/cm² and for 20 minutes, with colloidal substance, $\times 280$

Photo. 3
Colloidal substance on Pb, $D_a = 20$ mA/cm², for 10 minutes, $\times 280$

Photo. 4
Structure of Cd electropolished at 10 mA/cm² and for 10 minutes, showing grain size, $\times 280$

Photo. 5
Sn surface electropolished at 15 mA/cm² and for 10 minutes, $\times 280$

Photo. 6
Structure of Ag electropolished at 14 mA/cm² and for 20 minutes, $\times 280$

Photo. 7
Structure of Bi electropolished at 10 mA/cm² and for 40 minutes, showing fine grain size, $\times 280$

Photo. 8
Fused-like surface of Mn electropolished at 14.5 mA/cm² and for 10 minutes, $\times 280$

voltage increased rapidly (Fig. 3).

Ni surface was not electropolished in this experiment* and the anodic current efficiency determined by the coulometric measurement based on the reaction $\text{Ni} \rightarrow \text{Ni (II)}$ was approximately 12% at current density of 30 mA/cm² and at resulting voltage up to 15.2 V, gas evolution being accompanied.

During electrolysis of Co, Pb, Cd Sn and Ag, the viscous layer or mossy precipitates were observed. Photo. 2~6 show the appearance of the electropolished surfaces by microscopic observation.

In the case of Pb, a polished surface was not obtained in the range of 100 mA/cm². Pb surface changed into dark color at 3 mA/cm² and a small quantity of gas and sticky viscous layer were observed at 10~100 mA/cm². Photo. 3 shows a colloidal substance on Pb after electrolysis at 20 mA/cm² and 10 minutes.

In the case of Bi, at 10 mA/cm² the surface was electropolished with approximately 96.5% efficiency based on the reaction $\text{Bi} \rightarrow \text{Bi (III)}$, and beyond 20 mA/cm² accompanied with gray solid substance.

In the case of Mn, the metal dissolved spontaneously in the solution with gas evolution, however upon anodic polarization gas evolution ceased and electropolished surface appeared at the limiting current density of ca. 5 mA/cm².

Photo 7, 8 show the appearance by microscopic observation. In Table 1 appropriate conditions of electropolishing of some metals were summarized.

Baba²², one of authors, previously studied on electropolishing of metals in the nonaqueous system $\text{NH}_4\text{SO}_3\text{H}-\text{HCONH}_2$, the metals electropolished; being Cu, Zn, Cd, Pb, Fe, Ni, Mo, Ag, Mn, Ti, brass and 18-8 stainless steel.

Table 1 Appropriate conditions of electropolishing of some metals

D_a (mA/cm ²)	Cell voltage (V)	Remarks
Mn 10~25		<8 mA/cm ² , gas evolution >10 mA/cm ² , brightening
Ag 3~50	3.5~36	0.2~3 mA/cm ² , mossy layer
Cd 8~30	7.3~29	>20 mA/cm ² , brown viscous layer >30 mA/cm ² , unstable cell voltage
Sn 6~30	2.2~18	>30 mA/cm ² , sticky viscous layer
Mo 20~80	18~63	brown viscous layer
Bi 5~20	5.2~19	>10 mA/cm ² , unstable cell voltage >20 mA/cm ² , gray solid film
Co 5~10		>10 mA/cm ² , mossy layer and gas evolution

* Under the particular conditions, that is, at much higher current density in saturated acid concentration (ca. 2M), pitting and brightening both accompanied by gas evolution were observed at 80 mA/cm² for the former and 320 mA/cm² for the latter.

The electropolishing conditions, indicated by Baba, were 250 mA/cm² of anodic current density and 1M-sat. (ca. 2.9) acid concentrations. Formamide solutions appear to be superior to aqueous solutions and to dimethylsulfoxide solutions with respect to electropolishing since a many kinds of metals including Ti and 18-8 stainless steel could be polished. Moreover, Menzies et al.²³ succeeded in electropolishing of W and U in formamide solutions.

It should be noted that higher current density was required for electropolishing as compared with the current densities employed in dimethylsulfoxide solutions.

As indicated by Menzies et al.²³, it is unlikely that the viscous layers observed in both nonaqueous solutions are hydroxides or oxides. Gas evolution at higher current densities and anodic dissolution efficiencies indicate the occurrence of side reactions. In the case of formamide solutions, the reaction between sulfamate anion and solvent results in HCNO gas evolution²⁴.

It seems that the gas evolved from dimethylsulfoxide solutions is composed of complicated constitutions produced by the reactions between sulfamate anion and solvent. Further investigations on the composition of gas and viscous layers should be needed.

3.4 Anodic current efficiency, cell voltage and cell resistance

Anodic current efficiency of some metals determined by coulometric measurement and experimental conditions for electropolishing were shown in Table 2.

Table 2 Current efficiency of anodic dissolution

	D_a (mA/cm ²)	Cell voltage (V) initial final	Efficiency (%)	Remarks
Mo	30	26~28.5	89.9	Mo→Mo (VI)
Sn	30	10~18	97.3	Sn→Sn (II) unstable cell voltage
Cd	30	17~28.5	100	Cd→Cd (II) same as above
Pb	30	29~28	94.2	Pb→Pb (II)
Bi	20	19~24	96.5	Bi→Bi (III)
Ni	30	13.3~15.2	11.9	Ni→Ni (II) periodic oscillation of cell voltage before complete passivation
Ag	4	4.2~3.9	96.8	Ag→Ag (I)
"	8	5.7~4.9	100	
"	20	11.8~9.5	96.6	unstable cell voltage
"	37	15.3~28.3	95.2	cell voltage rose up
"	45	17.3~46.5	97.3	rapidly after induction
"	77	29.5~60.3	98.0	time

The cell voltage-cell resistance-current density are typically shown for Ag and Pd in Fig. 5.

The cell resistance maximum was observed in the

Fig. 5 Relationships of cell voltage-current density (.....) and cell voltage-cell resistance (—) for silver and lead
○ : Ag, × : Pb

case of Pb, Cd, Sn and Ag. Cell resistance is generally high owing to the low conductivity of sulfamic acid-dimethylsulfoxide system.

The resistance maximum is evidently due to the formation of the loosened layer which fell down during electrolysis.

Cell voltage increased slowly with increasing current density in the beginning. Cell resistance, however, decreased rapidly with increasing current density at the start, then increased due to the formation of viscous layer accompanied with the rapid increment of cell voltage.

The dissolution efficiency of Ag was approximately 95.2~100% (4~78 mA/cm²) based on the reaction Ag→Ag (I). During electrolysis, cell voltage rose up abruptly after induction time in the cell voltage-time curve and instability of cell voltage were observed beyond 30 mA/cm².

It was considered that the oscillation of cell voltage came from the break down and formation of solid layer caused by the saturation of metal ion.

4 Summary

Anodic behavior of 11 metals (Mn, Ag, Cd, Sn,

Pb, Mo, Bi, Co, Ni, Ti and Ta) were investigated in 1.0M sulfamic acid-dimethylsulfoxide solution.

The properties of Ag/Ag⁺ electrode used as reference electrode were examined and its availability was confirmed. The recovery time after polarization to ± 50 mV was sufficiently fast and its reversibility was comparable to aqueous Ag/Ag⁺ electrode.

7 metals except for Pb, Ni, Ti and Ta were electropolished and the viscous layer was observed. Although Pb dissolved anodically with approximately 94.2% efficiency based on the reaction Pb→Pb (II), there appeared always a colloidal substance on the surface.

The dissolution efficiency of Ni was ca. 12% based on the reaction Ni→Ni (II). It could be suggested from the low efficiency, high overvoltage and from the appearance of the metal after electrolysis that a passive oxide film, which had a fairly high conductivity for nickel cation and electrons, was formed.

In the case of Ta, an interference film was formed at 5 mA/cm², whereas in the case of Ti, arcing was observed at 10 mA/cm².

The cell resistance maximum accompanied with the increment of cell voltage was observed in the case of Pb, Cd, Sn and Ag, which suggested the occurrence of viscous or solid layer on the anode.

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