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Corrosion Studies of Metals in Molten $\text{AlCl}_3\text{-NaCl}$

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Abstract

Anodic polarization curves of various metals and alloys in molten salt mixtures of aluminium chloride-sodium chloride at 200°C were measured by using the potential sweep method at a sweep rate 2.50 mV/sec. The anodic polarization curves obtained from different metals are classified into three types by their shape; (i) Monotonic rise of the anodic dissolution current with the potential for Aluminium, Silver, Copper and Molybdenum. (ii) Characteristic passivation for Nickel, Palladium, Titanium, Iron, Stainless Steels and Platinum. (iii) Chlorine gas evolution without anodic dissolution for Tungsten. The effects of composition of Ni-Cu alloys on the corrosion rate, corrosion potential and anodic peak current in the melt were examined, and the corrosion rate of the alloy was found to decrease with increasing Ni content, particularly for the alloys with a more than 30% Ni content.

Part I. Anodic polarization curves of metals and alloys in molten $\text{AlCl}_3\text{-NaCl}$ at 200°C.

1. Introduction

Few kinetic studies on the corrosion of metals in molten salts in the literature are available. Janz and Conte¹⁾ measured the potentiostatic polarization curves of stainless steels and several noble metals in molten alkali carbonates at 600°C. Pizzini et al.²⁾ found that there was no activation overpotential either in anodic or in cathodic reactions on a nickel electrode in molten alkali fluorides free of oxide, though the nickel electrode became a layer-covered electrode during anodic polarization when the melt contained a trace amount of oxygen. In molten chloride systems Piontelli et al.³⁾ also observed no activation overpotential in the dissolution and deposition processes of various metals (Ni, Mg, Al, Pb, Sn, Cd and Zn) in their chloride melts mixed with potassium chloride. Tomashov and Tugarinov⁴⁾ measured the anodic and cathodic polarization curves of iron and the effect of oxygen ions and cations in the melt on the corrosion rate of iron in either of pure KCl, NaCl or CaCl_2 at temperatures ranging from 700° to 900°C, and discussed the corrosion mechanism. Takahashi and Amada⁵⁾ measured the anodic

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polarization characteristics of various metals (Au, Pt, W, Ni, Ag and Cu) in a molten LiCl-KCl system at 450–500°C and suggested that the dissolution process was controlled by the diffusion of the metal ion in the melt. Most of the polarization measurements in the studies described above have been made in temperatures higher than 400°C.

In the present paper, the measurements were performed to gather information about the anodic dissolution of 13 kinds of metals in molten mixtures of AlCl_3 and NaCl. This melt is relatively easy to handle because it is transparent, stable and has a low melting point (mp. of an eutectic composition 112°C), though the highly volatile and hygroscopic nature of AlCl_3 produces a little difficulty.

2. Experimental

The molten mixture of AlCl_3 and NaCl was prepared from purified AlCl_3 by a multi-sublimation process and NaCl of analytical grade dried for several days in a drying oven at 150°C before use. Further purification was made by a reduction treatment of the melt with small pieces of aluminium metal for several days at 200°C. The melt tends to be slightly blackish by the addition of aluminium to the melt. The black colloids appeared and increased in size by coagulation with the extended time of reduction treatment. The floatings are considered to be impurities containing carbon or silicon. The transparent melt obtained was solidified in test tubes and stored in a desiccator. The salts were remelted and placed

in a cell for use. The apparatus and the electrochemical cell used are schematically shown in Fig. 1. The cell with four openings was made of Hario-glass (net content 200 ml). The reference electrode was a high purity aluminium wire (Si 0.0006%, Fe 0.0006%, Cu 0.0003%, 2 mm in diameter) immersed in the melt located in a fritted glass compartment. A larger part of the cell was immersed in a silicon oil bath which made visual observation of specimens during the experiment possible. The temperature was kept constant at $200 \pm 1^\circ\text{C}$ by stirring the bath. The specimen of the metals used were 99.9–99.99% pure wires (1–3 mm ϕ) except for stainless steels. They were abraded with an emery paper No. 0/4, degreased with benzene, dried in air and partially immersed in the melt.

Anodic polarization measurement was carried out by means of the po-

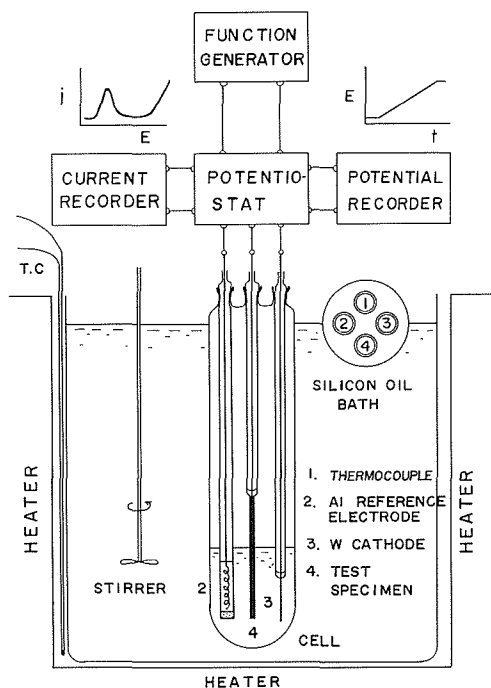


Fig 1. Schematic diagram for anodic polarization measurement and assemblies of the electrochemical cell.

tential sweep method used in stagnant melts. The electrode potential was shifted in the anodic direction from a corrosion potential at a constant rate of $dE/dt = 2.50 \text{ mV/sec}$ and anodic current with the potential were recorded automatically. All electrode potentials were measured against the aluminium reference electrode.

3. Results and Discussion

The composition of the melt changes gradually with time because of sublimation of AlCl_3 which is deposited at the low temperature side of the cell. (Vapor pressure of AlCl_3 in the eutectic composition is about 35 mmHg at 200°C). The corrosion potential of Al depended scarcely on the melt composition and its value measured was $-2.10 \text{ V} \pm 8 \text{ mV}$ against the chlorine electrode in the melt of 55–60 mol % AlCl_3 .

The corrosion potentials measured in 13 kinds of metals after 10 min, immersion were listed in Table 1; the measurement was made within an error of 0.14 V. It may be seen in the table that the potential depends on the nature of the metals and that the active metal does not always have a potential less noble than that of noble metals. It should be noted that the corrosion potentials of Cu and Ag are almost the same, and that Mo and W also have the same potentials.

Table 1. Corrosion potentials of metals in $\text{AlCl}_3\text{-NaCl}$ melt at 200°C .

Metals	E (V v.s Al reference electrode)
Al	0.00
Ti	0.11 ± 0.02
Zn	0.29 ± 0.01
Ag	0.61 ± 0.02
Cu	0.62 ± 0.02
Fe	0.66 ± 0.04
Ni	0.88 ± 0.04
304 Stainless	0.85 ± 0.05
316 Stainless	0.89 ± 0.04
Pd	1.52 ± 0.03
W	1.63 ± 0.06
Mo	1.69 ± 0.06
Pt	1.77 ± 0.07

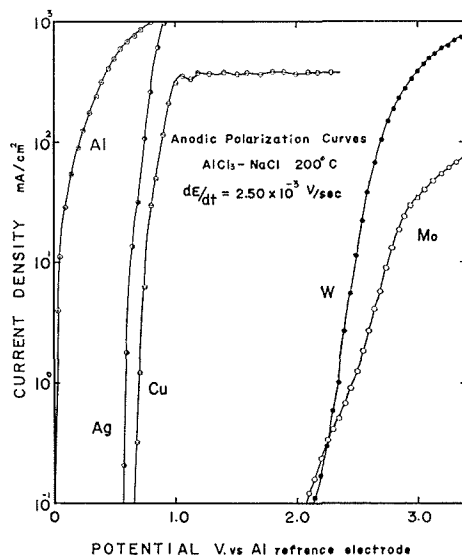


Fig 2. Anodic polarization curves for silver, aluminium, copper, tungsten and molybdenum.

In the anodic polarization starting from the corrosion potential the anodic current of Al, Ag, Cu, W and Mo, as seen in Fig. 2, increased with the potential and finally reached a limiting current i_L . The i_L of copper was about 300 mA/cm^2 under stagnant conditions. The melt changed to brown by dissolution of Cu and

to pink by Mo, while there was no change in color by dissolution of Ag and Al. Mo dissolved into the melt evolving chlorine gas from the surface of Mo electrode in the potential region above +2.20 V. Grain boundaries of Mo and Al specimens were etched by dissolution. In the anodic polarization of W, the chlorine gas was evolved exclusively on the surface, and no amount of dissolved W were detected in the melt after polarization. Moreover, since there was no visual change in the W-electrode surface after the polarization, the anodic current may be surmized to be due to the chlorine gas evolution.

Two current peaks at +0.25 V and +1.30 V in the anodic polarization curve of Ti were observed, as shown in Fig. 3. The peak current at the lower potential was about one seventh of that at the higher potential. Ti dissolved at the potentials of two current peaks. At the potential of about +1.40 V the Ti electrode was covered with dark-violet corrosion products, probably titanium trichloride. The current decrease observed at potentials above +1.30 V would be due to the ohmic resistance of the corrosion products. There appear to be several different types of reactions in the anodic process of Ti.

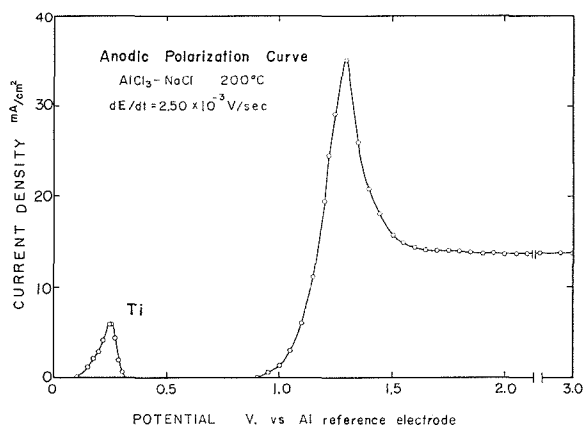


Fig 3. Anodic polarization curve for titanium.

The anodic polarization characteristics of Fe, 304 type and 316 type stainless steels, and Pt are shown in Fig. 4. Fig. 5 shows the anodic polarization curves of Ni and Pd. These metals exhibit passivation as seen in Ti. In the potential above the dissolution peak of Fe at +0.78 V, the anodic current of Fe increased slightly at the potential around +2.40 V. The chlorine evolution on the surface was not observed up to the potential of +3.50 V. Stainless steels, 304 type and 316 type, showed almost the same polarization curves with a sharp current peak at about +1.00V, which is a more noble potential than that of Fe, and a small peak was seen at +2.00 V followed by a steep current increase at +2.40 V producing chlorine gas from the surface. The onset potential of dissolution of Pt was at +1.89 V, which is less noble than that of the potential of chlorine evolution. Midorikawa⁶⁾ observed an inflection of anodic current at +1.86 V, lower than the potential of chlorine evolution, in the galvanostatic $E-i$ curves. Free

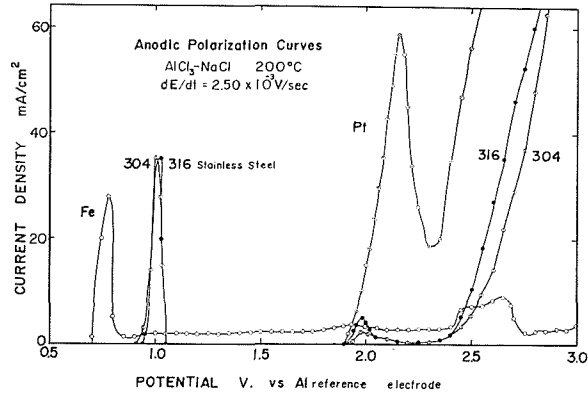


Fig 4. Anodic polarization curves for platinum, iron, and stainless steels of two types 303 and 316.

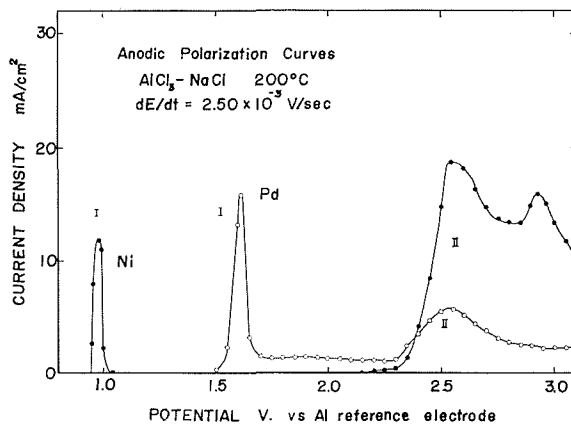


Fig 5. Anodic polarization curves for nickel and palladium.

energies of formation of PtCl_2 and PtCl_4 give equilibrium potentials at +1.71 V and +1.81 V, respectively, which are in good agreement with the onset potential of dissolution. This inflection was determined to be a dissolution of Pt used as the anode in this experiment. Several current peaks of Pt in KCl-LiCl melt at 400–600°C investigated by Takahashi et al.⁷⁾ were not observed in this work.

The anodic dissolution and passivation were observed to occur on Ni and Pd; this will be referred here as the first peak. The anodic current of Pd increased again at about +2.30 V (The second peak). Reproducibility of the anodic current of nickel was not acceptable in a potential range more noble than +2.50 V. On the other hand the second rounded hump of Pd was relatively reproducible compared with the first one. The second peaks might be related to the chlorine evolution reaction. It is noted that there is some correlation between the corrosion product accumulated by the anodic dissolution and the higher overvoltage of chlorine evolution. The metals covered by corrosion products, such as Ni, Pd and Pt, had a potential of chlorine evolution at +2.30~+2.40 V at which time

the anodic current rises steeply producing Cl_2 gas on the metal. With the metals uncovered by the corrosion products, such as W, however, the Cl_2 evolution potential was +2.10 V in coincidence with the theoretical Cl^-/Cl_2 electrode potential. The maximum of anodic dissolution current i_p (mA/cm^2) depends upon the potential sweep rate in a range of $dE/dt=2.50\sim 3.30\times 10^{-2}$ mV/sec. The plot of i_p of nickel against $(dE/dt)^{1/2}$ gives a straight line, which indicates that the reactions are diffusion controlled. The i_p increased in the order of $\text{Ni}<\text{Pd}<\text{Fe}<\text{stainless steels}<\text{Pt}$, though the current values obtained are rather scattered. The i_p increased with the temperatures, and the activation energy estimated for i_p of nickel was 5.1 kcal/mol.

The passivation phenomenon of Ni should be different from that of Ti, since there was no change on the Ni surface and some corrosion products were seen on the surface of Ti. Ni seems to be covered with a passivation film that may be composed of nickel hydroxide or nickel oxide rather than of nickel chloride. It is possible to form nickel oxide NiO by the reaction of Ni and trace amounts of O^- present in a fused salt⁸⁾. The existence of nickel-oxichloride has not been confirmed in fused chloride, as reported by Laitinen and Bhatia⁸⁾. The possibility of existence of a higher oxide such as Ni_2O_3 on nickel in alkali sulfate melt was reported by Hill et al.⁹⁾

In the corrosion test Ni dissolved in the melt without passivation when it was kept in the AlCl_3 -NaCl melt for hours. The fused salt containing Ni^{2+} ions showed yellow-green, the same color of NiCl_2 dissolved in the melt at 200°C, while at higher temperatures above 400°C it turned blue, and the change in color with temperature was reproducible. The fact suggests that different types of nickel chloride complexes will be formed depending on the temperature. The solubility of anhydrous NiCl_2 increased with the AlCl_3 concentration in the melt. Further work on the complex formation of nickel chloride in this media is in progress at our laboratory. In our experiments W and glassy carbon were found to be suitable materials for the chlorine gas electrode in the melt, but Pt, Mo and a spectroscopic grade graphite were not suitable because of swelling.

4. Conclusion

Anodic polarization measurement was made by the potential sweep method on 13 kinds of metals in molten AlCl_3 and NaCl at 200°C. It was concluded that there are three modes of polarization curve in the anodic reaction of metals; (i) Monotonic rise of anodic dissolution current with the potential observed of Al, Ag, Cu and Mo. (ii) Passivation characteristics observed of Ni, Pd, Ti, Pt, Fe and stainless steels. (iii) Chlorine gas evolution without any anodic dissolution observed in W and glassy carbon. The passivation of metals in fused chloride is thought to be due either to metal chloride formation, or to metal oxide and/or to metal oxi-chloride formation. With a sufficient high current density it is possible to passivate the metals belonging to (ii) as stated above, by making these metals anodic in the melt.

Part II. Effect of nickel content on the corrosion of Ni-Cu alloys in molten $\text{AlCl}_3\text{-NaCl}$.

1. Introduction

An investigation of the corrosive action of the chloride melts to metals are of theoretical and practical interest. Corrosion studies in molten salts are lacking in the literature. This study deals with corrosion tests, measurement of the peak currents in the anodic polarization curves and the corrosion potentials of Ni, Cu and Ni-Cu alloys in the $\text{AlCl}_3\text{-NaCl}$ melts. Ni and its alloys are fairly resistant to the action of alkali chloride melts at high temperatures.

2. Experimental

(i) Corrosion tests

The metals and alloys specimens were all 2 mm in diameter and 30 mm in length; the chemical compositions are shown in Table 2. Corrosion tests were carried out with the apparatus shown in Fig. 6. The molten salt was contained in a glass capillary (250 mm in length, 3.5 mm in diameter, with a small hole (2 mm ϕ) from the bottom), in which the test specimen was completely immersed in the melt. The molten salt preparation was the same as described earlier. (Part I) The specimens were first abraded by No. 0/4 emery paper rinsed with methanol, dried in air, then weighed prior to use. After the test for a required time (16 days), the specimens were quickly removed from the melt and plunged into water to dissolve the salts on the specimen. The corrosion losses of the specimens were determined from the difference in weights of the specimens before and after the experiments.

Table 2. Chemical Composition of the Metals and Alloys Tested

Content (wt. %)					
Cu	Ni+Co	Mn	Si	Fe	C
0.005	99.45	0.18	0.03	0.08	0.04
31.32	66.25	1.02	0.15	1.18	0.08
56.52	42.02	0.89	0.04	0.50	0.03
69.75	29.86	0.20	0.04	0.12	0.03
78.43	20.86	0.45	0.04	0.18	0.04
99.94	—	—	—	—	0.03

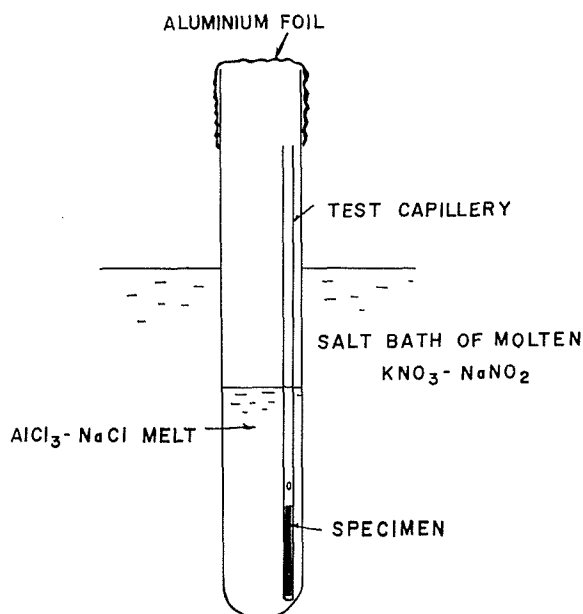


Fig. 6. Apparatus for Corrosion test.

(ii) The anodic peak current i_p and the corrosion potentials E_{corr} of the specimens.

The potential sweep method was used to determine the anodic peak current

i_p of the metals and alloys in the molten salts at a constant sweep rate of 9.25 mV/sec. The corrosion potentials E_{corr} of the specimens which became steadily established after 5 minutes immersion were measured by using a bulb potentiometer. The specimens were partially immersed in the solution.

3. Results and Discussion

Fig. 7 shows the corrosion rate of the specimens in the melts at 220°C (a) and 240°C (b). As seen in the figure the corrosion rate of the metals and alloys decreased with increase of Ni content, particularly in the Ni content region higher than 25 wt%. The corrosion losses increase with rise of temperature. The difference of corrosion rates between two results (a) and (b) in Fig. 7, however, seems to depend not only on the working temperature but on the trace of moisture in the original melt. The corrosion rate of copper was about 3 to 6 times as large as that of nickel in the molten AlCl_3 -NaCl at a temperature of 220–240°C. It has been previously that in molten alkali chloride free from AlCl_3 the difference of corrosion rate between that of copper and of nickel was not so large as the present result. The corrosion rate of nickel was 0.1 mg/cm²·hr in molten KCl or NaCl, and 1.3 mg/cm²·hr in molten LiCl, while that of copper was 0.3, 0.4, 1.6 mg/cm²·hr in molten KCl, NaCl and LiCl at 800°C, respectively¹⁰. The anodic polarization curves of nickel and Ni-Cu alloys show the maximum current i_p for the passivation, but not for pure copper in the melt. Fig. 8 shows the corrosion potentials E_{corr} as well as the anodic peak currents of the metals and alloys in

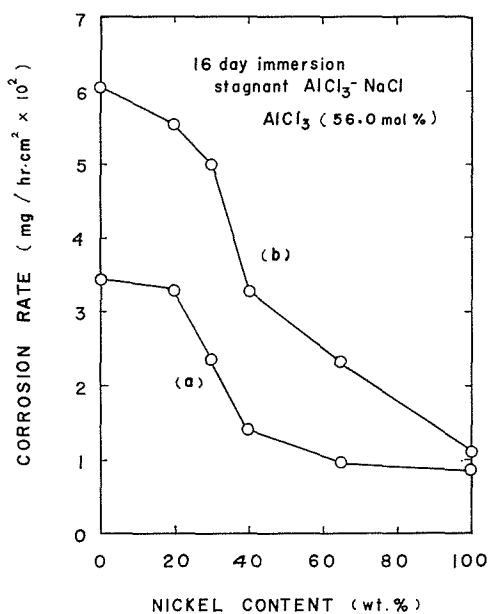


Fig. 7. Dependence of corrosion rate of the specimens on nickel content of the alloys in AlCl_3 -NaCl melt at 220°C (a) and 240°C (b).

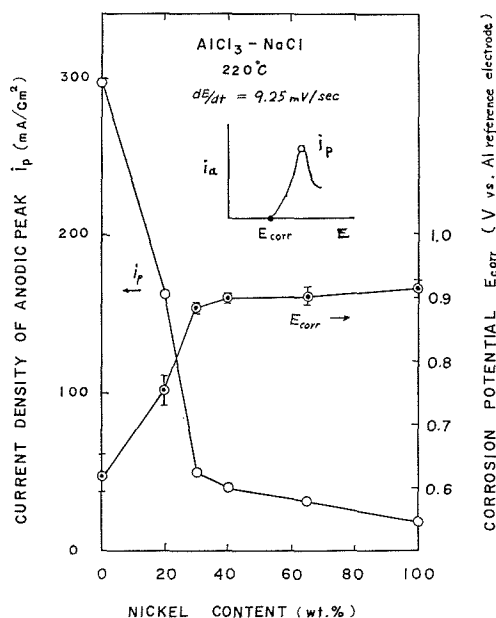


Fig. 8. Dependence of i_p and E_{corr} on nickel content of the alloys in AlCl_3 -NaCl melt at 220°C.

the melt at 220°C. E_{corr} decreased and i_p increased considerably in alloys with less than 30% Ni content, while for those of Ni content from 30% to pure Ni both E_{corr} and i_p do not depend so much on the composition of the alloys. The Ni content of Ni-Cu alloys has almost the same effect on the i_p and on the corrosion rate in the tests. The amount of charge for passivation, obtained by integration of the anodic current, would be another reasonable measure of corrosion resistance of the metals and alloys, which is related to the amount of dissolution of the metals and alloys by Faraday's law.

4. Conclusion

- (1) The effect of the composition of Ni-Cu alloys on the corrosion rate, on the corrosion potential E_{corr} and on the anodic peak current i_p in the molten mixture of NaCl and AlCl_3 was investigated.
- (2) The Ni-Cu alloys showed anodic passivation characteristics such as seen nickel in melt at 220°C.
- (3) It was shown that the Ni content of the alloys affects the corrosion rate, the E_{corr} and the i_p in the melt for the alloys containing Ni less than 30 wt % to an appreciable extent.

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