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FUNDAMENTAL STUDIES OF METAL FLUORINATION REACTIONS

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ABSTRACT

Solid-state electrochemical methods are being used to determine structural, thermodynamic, and transport properties in materials pertinent to the fluorination of metals at elevated temperatures. The solubility and diffusivity of fluorine in solid metals (initially nickel) are being studied by a potentiostatic electrochemical procedure by which changes in an impressed cell voltage induces changes in the activity of fluorine at a metal/electrolyte interface while the recording of the resulting cell current as a function of time can be interpreted to yield the desired quantities. Defect structures in metal fluoride compounds (initially NiF_2 and PbF_2) are being studied through measurements and interpretation of the electrical conductivity. The variation in the conductivities of the pure and impurity-doped compound as a function of fluorine activity can be interpreted to establish the partial ionic and electronic conductivities of the compound, and the concentrations and mobilities of the carriers. Finally, a CaF_2 -electrolyte probe (gauge) is being developed for the measurement of fluorine activities in gases at elevated temperatures.

During the first nine months of this contract, the literature has been searched and studied. Experimental materials have been ordered and two high-temperature electrochemical systems have been constructed and tested. The electrical instrumentation has been tested and calibrated. A porous graphite electrode was found to be effective in fixing and transmitting fluorine activities which are set electrochemically at one graphite/electrolyte interface. This preliminary success establishes the intended means for the variation of fluorine

activity in the electrical and conductivity measurements. Co-existence electrodes of nickel plus nickel fluoride at 850-950°C have been found to remain essentially reversible despite current passage up to significant current densities. These results will permit the conduct of the intended potentiostatic coulometric titration measurements. A preliminary fluorine probe design will soon be tested.

INTRODUCTION

The present research is being undertaken to study some fundamental thermodynamic transport properties and detailed mechanisms pertinent to metal fluorination reactions. The program consists of determining the following properties using solid-state, CaF_2 -electrolyte galvanic cells: (A) solubility and diffusivity of fluorine in metals, specifically nickel, and (B) the nature of the point defects (type, concentration and mobility) in metal fluorides as a function of fluorine partial pressure, temperature and impurity concentration. The latter study encompasses the study of the electrical conductivity of metal fluorides under thermodynamically well-defined conditions.

Another objective of the program is: (C) to design and construct a fluorine probe for the measure of fluorine chemical potentials in gaseous environments. The probe must be evaluated in atmospheres that are reactive to fluorides and which might thus limit its accuracy and lifetime.

A. Determination of Diffusivity D_F and Solubility N_F of Fluorine in Nickel (S. Reddy)

A potentiostatic electrochemical experiment involving the CaF_2 solid electrolyte is proposed for the determination of diffusivity and solubility of fluorine in nickel. The method is similar to that used by Pastorek and Rapp¹ for the determination of solubility and diffusivity of oxygen in solid copper using the oxygen-ion-conducting zirconia electrolyte. The experimental method consists of a double cell arrangement shown in Figure 1.

The nickel electrode is a thin "pill" of high-purity nickel which is tightly bonded to the interfacing CaF_2 electrolyte pills. Initially, the potentiostat is set on an electromotive force E_1 and the nickel is brought to equilibrium at

at a well-defined fluorine activity somewhat below the $\text{Ni} + \text{NiF}_2$ coexistence activity. At the start of an experimental run, the electromotive force is jumped to a new value, E_2 which results in a new fluorine activity at the nickel/electrolyte interfaces. The diffusion of fluorine atoms in Ni metal is monitored by a continuous measurement of cell current. From the solution of the diffusion equation and the time-dependence of the current, values for the solubility and diffusivity of fluorine in solid nickel can be derived.¹

In order that the experiment be successful, the following conditions must be satisfied: (a) the CaF_2 electrolyte should exhibit completely negligible electronic conduction under the experimental conditions; (b) over the range of ionic currents associated with fluorine diffusion into or out of solid nickel, the $\text{Ni} + \text{NiF}_2$ reference electrodes should remain unpolarized. i.e., under current passage, the equilibrium fluorine activity at the interface between the $\text{Ni} + \text{NiF}_2$ electrode and the CaF_2 electrolyte should remain undisturbed.

Available data indicate that the CaF_2 electrolyte exhibits completely negligible electronic conduction. In the current study, preliminary experiments have been conducted to determine the polarizability of $\text{Ni} + \text{NiF}_2$ reference electrodes in combination with pure CaF_2 electrolytes; the results of these experiments will be described presently.

Experimental Details

Materials:

Ultrapure CaF_2 powder
Anhydrous NiF_2 powder
Nickel powder-100 Mesh

All these materials were purchased from Ventron Corporation=Chemical division.

Electrode and Electrolyte Preparation

The co-existence electrodes were prepared from a Ni metal and NiF_2 mixture in a volume ratio of approximately 4 to 1. The two powders were mixed by grinding in a porcelain mortar and pressed in a steel die to form 1.3 cm dia. pellets at 10,000 lbs load. The CaF_2 electrolyte discs were also made by pressing at the same load. The mixing and loading into the die was done in a dry box filled by an argon atmosphere.

Electrode Lead Material

In the literature, various metals such as molybdenum, tantalum, nickel and platinum wires have been used to provide electrical contact between the fluoride electrodes and the external circuit. As a basic requirement for the electrical lead wire, it should not react with the fluoride at the high temperatures of the experiment. Because nickel has a low scaling rate in fluorine and is comparatively inexpensive, Ni wire was used in the present experiments as the electrical contact between the two reversible electrodes and the external circuit.

Gas Purification Train

The fluorides react very readily with oxygen and water vapor at high temperatures resulting in the formation of oxides. Hence it is essential to maintain an inert atmosphere free of oxygen and water vapor.

In the present experiments, argon purified of O_2 and H_2O was used as the inert atmosphere in a fluoride cell. Figure 2 illustrates the Ar-gas purification train employed.

Experimental Apparatus

Figure 3 is a schematic illustration of the apparatus with the cell in place. The electrode and electrolyte pellets were pressed together between

nickel sheets by a spring-loaded Al_2O_3 pushrod. The nickel lead wires were spot-welded onto the nickel sheets and insulated from each other through the Al_2O_3 tubes. The temperature of the cell was measured using a Pt/Pt-10%Rh thermocouple. The cell leads and the thermocouple wires were taken out of the cell through the brass head by using glass to metal (Kovar) seals.

The cell was heated in a Kanthal-wound resistance furnace. The temperature was controlled within $\pm 1.5^\circ\text{C}$ using a Barber-Coleman controller. A grounded stainless steel tube surrounded the outer mullite tube to prevent external electrical noise from affecting the emf measurements.

Experiment to Study the Polarizability of Ni + NiF_2 Electrodes

The polarizability of the Ni + NiF_2 electrodes was studied using the cell shown in Figure 4.

The electrolyte and the electrode pellets were stacked together between Ni-sheets and placed inside the cell. The cell was flushed for half an hour with purified argon and then evacuated. The cell was then heated under a vacuum of 10^{-7} torr, maintained at 500°C for 4 hours and then filled with Ar and heated to desired experimental temperature. All measurements were done in flowing purified Ar-gas.

Constant d.c. currents were passed through the symmetric cell $\text{Ni-NiF}_2 \mid \text{CaF}_2 \mid \text{Ni-NiF}_2$ in the temperature range $850^\circ\text{--}950^\circ\text{C}$. The current was controlled using a Keithley 240 regulated high-voltage supply which was connected in series with a variable resistor. The current was measured using a calibrated Keithley 153 microvolt-ammeter connected in series with the cell. The cell emf was measured with a Leeds & Northrup K-3 potentiometer to an accuracy of 0.01 mV.

At the start of each experimental run, the open-circuit voltage was monitored. Although this value should theoretically be zero, a value between 0.06 to 0.1 mV was observed because of a small temperature gradient across the cell. Such low values for $E_{o.c.}$ did not affect the study of electrode polarization. After the circuit was closed, the voltage drop across the cell was monitored at intervals of 2 to 3 minutes for 15 minutes. For small currents, the cell voltage became constant within one minute and did not change with time. After the current flow was interrupted, the voltage returned to the original thermal emf value within a short period of time. The measured voltages were corrected for the small open-circuit values at each temperature.

RESULTS

The results of the experiments at 850, 900 and 950°C are plotted in Figures 5, 6 & 7 as current vs voltage. The measured voltage drop (V) across the cell is given by

$$V = IR + \eta$$

where I is the current, R is the cell resistance and η is overvoltage.

In order to check the absence of polarization, a direct measurement of the cell resistance was made by taking the oscillographs of the change in cell voltage during the initial fraction of a second after the current was applied. The IR drop across the cell is instantaneous, while the overvoltage is a time-dependent contribution. As a further check, the resistance of the cell was measured using an a.c. Wayne-Kerr bridge at a fixed frequency of 1592 cycles/sec. Values of R obtained from the plots of current vs voltage and the resistances determined from the oscillograph and ac bridge method are compared in the following table:

Temperature °C	Current Range μ a	R ohms I-V plot	R ohms Oscillograph	R ohms ac bridge
850	0-50	195	198	180
900	0-100	74	80	48
950	0-300	15.7	13.4	---

Resistances obtained from I-V plots are in good agreement with those obtained from the oscillograph. However, the resistance obtained by the a.c. bridge method is less than those obtained by the other two methods. A better comparison would require the extrapolation of the a.c. resistance to zero frequency; however, the differences still seem to be large and the reason for this is not clear at this time.

According to the above table and Figures 5-7, in the current ranges studied, overvoltage is negligible (the plots are linear) and the Ni + NiF₂ electrodes behave reversibly. Hence Ni + NiF₂ electrodes can be used for the potentiostatic determination of solubility and diffusivity of fluorine in nickel, provided that the ionic currents do not exceed the range indicated.

FUTURE EXPERIMENTS

The extension of this research to accomplish the coulometric titration of fluorine into nickel, as described in the original proposal, has been initiated and will serve as the primary research objective for this task in the next year.

B. A Conductivity Study of Point Defects
in Pure and Doped NiF₂ (W. C. Fang)

The object of this research task is the measurement of the a.c. conductivity of NiF₂ and doped-NiF₂ at known fluorine activities to test point defect models for the characterization of the type, concentrations and mobilities of the ionic and electronic defects in NiF₂.

Experimental Details

1. Gas Purification System

Because nickel fluoride may be less stable than nickel oxide in an impure gas system, specimens must be isolated from any exposure to oxygen, water moisture, and low-stability oxides. An effective gas purification system has been set up.

Argon gas (99.9%) is purified further by passing it sequentially over anhydrous magnesium perchlorate (Mg(ClO₄)₂), Drierite, ascarite, a column of copper oxide at 200°C, and copper turnings at 480°C, a cold trap refrigerated by liquid nitrogen, a bed of titanium sponge at 750°C, and finally through another cold trap. Figure 2 shows schematically the gas purification system.

- 1) Wool cotton: prevents fine particles from flowing out of the column.
- 2) Ascarite: to absorb water, CO₂ gas.
- 3) Magnesium perchlorate: absorption of water and volatile organic compounds.
- 4) Drierite: water absorber.
- 5) BTS copper catalyst: absorbs oxygen to form cuprous oxide which can be reduced by passing hydrogen gas at 150°C.
- 6) Copper turnings: absorbs oxygen and sulfur.
- 7) Cold trap: traps liquid particles and water vapor.

- (12) Furnace: used to heat titanium sponge to 750°C.
- (13) Quartz tube: used for storing titanium sponge heated in furnace at around 800°C.
- (14) Titanium sponge: oxygen getter.
- (15) Diffusion pump: type MCF-60C diffusion pump.

The residual oxygen concentration after purification should be below the detectable level by either gas chromatography or mass spectrometry.² However, a measurement of oxygen activity could be accomplished by use of a closed-end zirconia-base electrolyte cell.

2. Vacuum System

According to Figure 2, a Duo-Seal Model 1405-B mechanical pump and a Model MCF-60C diffusion pump were used to evacuate the system. The pressure of system reached less than 10^{-7} torr in five minutes. Pressure measurement is carried out by a cold-cathode vacuum gauge over the pressure range from 0.5 to 10^{-7} torr.

3. Flange and Specimen Holder Design

The experimental arrangement for the cell holder is shown in Figure 3. The cell assembly was designed to minimize the attack of any materials by fluorine vapor, and to permit the maintenance of a good vacuum. The cell was placed inside a 5 cm I.D. mullite tube, and pressed together by an alumina pushrod; the pressure on the cell can be adjusted by the springs in the cold zone. Nickel wires were used as electrical leads. Skelton and Patterson used nickel and nickel-alloy wire as leads.³ Some other metals have also been used: tantalum by Heus and Egan,⁴ molybdenum wires by Wagner⁵ and Benz.⁶ Nickel is one of the metals most resistant to attack by dry fluorine.

PRELIMINARY EXPERIMENT

In order to study point defects of NiF_2 , conditions of fixed and known, but variable fluorine activities will be needed. Use of a binary gas mixture

such as $\text{H}_2 + \text{HF}$ or $\text{H}_2 + \text{HCl}$ to control fluorine activities is unfavorable because of the attack of the experimental apparatus. Therefore an electrochemical arrangement is being used to establish fluorine activities. This preliminary experiment was conducted to establish whether this kind of electrochemical method could be used.

The cell (Figure 8) is made of two symmetrical cells with porous graphite in the middle. The coexistence electrodes were prepared from a nickel-nickel fluoride mixture in a volume ratio of approximately 4 to 1 and pressed in a 1.3 cm dia. steel die at 10,000 psi. The mixing and loading into the die were done in an argon-atmosphere dry box. Electrolytes were prepared from ultrapure calcium fluoride. Graphite disks were polished to one cm of thickness and wrapped with nickel wires as electrical leads. The time of exposure of the cell in air was no more than 4 minutes.

The cell system (Figure 8) was positioned in a grounded metal tube as electrical shield in a 1200°C resistance-heated furnace. The system was first evacuated at room temperature, then heated to 500°C in vacuo (10^{-7} torr), and then held for 18 hours at 800°C in an argon atmosphere. Voltages were applied by a Wenking potentiostat and measured by a Leeds & Northrup universal potentiometer. The results are shown in Table 2, which shows that the measured voltages are essentially the same as the applied voltages.

From these preliminary experiments, the control of fluorine activities can be achieved electrochemically by the application of cell voltages. This technique will be used in the future experiments, as the porous graphite disk electrodes can be used as good molecular fluorine exchangers. In future conductivity measurements, fluorine pressures will be maintained over a range from between 10^{-12} to 10^{-4} atmospheres. The equivalent applied voltage can be calculated through the relation

$$E_{\text{appl.}} = \frac{RT}{2F} \ln \frac{P_{\text{F}_2}}{P_{\text{F}_2} (\text{Ni} = \text{NiF}_2)}$$

Table 2. Test of Graphite Electrodes to Establish Fluorine Activities Set Electrochemically Through Applied Voltages

T = 800°C		T = 900°C	
$V_{\text{applied}}(\text{mv})$	$V_{\text{read}}(\text{mv})$	$V_{\text{applied}}(\text{mv})$	$V_{\text{read}}(\text{mv})$
32.8	33.2	203.9	203.5
171.5	171.5	203.4*	203.5*
175.6	176.0	379.4	377.7
205.5	206.0	374.9*	375.0*
369.2	369.0	511.5	507.8*
502.9	503.8	665.5*	665.3*
751.2	750.8	813.5*	813.7*
1019.8	1019.0	1027.5*	1027.7*
		1234.5*	1234.8*
		1513.8*	1517.2*

* reversed electrical polarity

Future Experiments

The success of this preliminary work promises the feasibility of using a similar arrangement for conductivity measurements on NiF_2 ; Figure 9 shows this arrangement. Applied voltages are established by using a potentiostat to establish fluorine pressures from 10^{-12} to 10^{-4} atmosphere. Measurements of a.c. conductivity will be made by using the Wayne-Kerr Universal Bridge B221. A Hewlett-Packard Model 201 Audio-Oscillator will be used to supply different frequencies (range from 20 CPS to 20 KC). The experimental temperature will be varied from 700°C to 1000°C.

Pure NiF_2 will be used in the first experiments, later doped- NiF_2 . On the basis of the fluorine pressure dependence of the conductivity of NiF_2 , the slope for the plot of conductivity versus fluorine pressure should provide information concerning the type of defects. From data for the hole mobility, a thermally activated "hopping electron" model and a "narrow-band conduction" can be diff-

erentiated by the differing expectations for the form of the temperature dependence.

The study of the electrical conductivity of pure and doped NiF_2 will represent the object of the experimental program for this task in the next year. This research is already underway.

C. An Electrochemical Probe for the Measurement of Fluorine Activities (S. F. Chou)

The stabilized zirconia electrolyte has been used in high-temperature electrochemical probes for the measurement of oxygen activities in either gaseous environments or liquid metals. An equivalent sort of probe should be possible for fluorine whereby the pure or doped CaF_2 electrolyte would be used. The open-circuit voltage of such a cell with a $\text{Fe} + \text{FeF}_2$ coexistence reference electrode would be given by

$$E = \frac{RT}{2F} \ln \frac{P_{\text{F}_2}(\text{gas})}{P_{\text{F}_2}(\text{Fe}+\text{FeF}_2)}$$

for which $P_{\text{F}_2}(\text{gas})$ is the fluorine activity of the gas phase. In the initial experimentation to test such a cell, the fluorine activity of the gas phase will be fixed by a $\text{Ni} + \text{NiF}_2$ coexistence mixture.

Because the CaF_2 electrolyte can react in an atmosphere containing sufficient oxygen to form CaO or to substitute oxygen into the CaF_2 structure, we have already encountered such problems in our present experimental work. However, in low-oxygen, fluorine-containing environments where CaF_2 is thermodynamically stable, the probe should prove effective.

Experimental Details

Oxides are generally more stable than fluorides because on their lower values of ΔG° formation per equivalent of compound. Therefore a dry box is used to store all the materials which are susceptible to oxygen contamination. Drying reagent and an argon environment minimizes the oxygen content in the dry box where all the operations involving the handling of fluorides are carried

out. Calcium fluoride was pressed into cylindrical pellets 1.3 cm in diameter by 2 to 3 mm thick under a pressure of 2000 lb/cm². A mechanical mixture of nickel and nickel fluoride powders was prepared and pressed into pellets of the same size as the calcium fluoride pellet. All fluoride pellets were sintered in an argon environment for 24 hours to prevent oxygen contamination. The two surfaces of the pellets were polished parallel to insure good contact.

The design of the cell is shown schematically in Figure 10. The assembly consists of two concentric mullite tubes. The two electrode chambers are separated by pressing the mullite tube (A) against the polished surface of the electrolyte block (B) which is CaF₂. The inner electrode pellet (C) Ni + NiF₂, is placed inside this tube and pressed against the electrolyte surface by means of a mullite pushing rod (D). The other electrode is gas phase of supposedly unknown P_{F2}. In these experiments, a pellet (E) of iron powder and iron fluoride mixture is settled in a mullite crucible (F) and is used to produce the fluorine atmosphere. The porous graphite electrode (G) with nickel wire connection is pressed against the outer surface of the electrolyte by means of the mullite crucible (F). This crucible is held in position by three nickel wires. The tension in this wire is maintained by three stainless steel springs at the cold end of the cell chamber. The entire assembly is placed inside a mullite tube of 5 cm ID and 45 cm long, which is connected to a brass tube through a Kovar joint. The brass part of the tube is connected to a brass flange by screws. A rubber O-ring is set between the two brass parts to ensure an air-tight seal of the cell chamber. The two electrode chambers are separately flushed with purified argon. A metal cylindrical tube is placed coaxially on the outside of the outer mullite tube and is grounded to prevent any a.c. pick-up during the emf measurement. All the Ni wires and the thermocouple wires in the cell chamber are insulated from the electrolyte by alumina capillary tubes.

A Leeds & Northrup type K-3 Universal potentiometer combined with a galvanometer is used to measure the emf with high precision. Two calibrated Pt-Pt/10%Rh thermocouples are used. One is placed close to the electrolyte to measure the cell temperature. The other is attached to a temperature controller to maintain the set temperatures within 0.5°C . The vacuum equipment and argon purification system are the same as described earlier.

Future Experiment

The availability of accurate thermodynamic data for a set of metal fluorides to be used as reference electrodes is a primary requirement in our work. Thermodynamic free energies of formation for CoF_2 , FeF_2 and NiF_2 were investigated by Chattopadhyay et al² and Skelton and Patterson.³ There was no substantial mutual solubility between CaF_2 and FeF_2 , NiF_2 or CoF_2 . These electrodes are recommended for use as reference electrodes in the fluorine probe. Open-circuit emf's will be measured to determine the fluorine activities in the environments equilibrated with these electrodes. A sequence of open-circuit emf values will be measured for differing fluorine activities as set by the different metal and metal fluoride mixtures.

Then, the argon atmosphere will be intentionally contaminated to a known and controlled oxygen activity to test the durability of the fluorine probe.

References

1. R. Pastorek and R. A. Rapp, Trans. Met. Soc. AIME, 245, (1969), 1711.
2. G. Chattopadhyay, M. Karkhanavala, and M. Chandrasekharaiah, J. Electrochem. Soc., 122, (1975), 325.
3. W. H. Skelton and J. W. Patterson, J. Less-Common Metals, 31, (1973), 47.
4. R. J. Heus and J. J. Egan, Z. Phys. Chem. N. F., 49, (1966), 38.
5. C. Wagner, J. Electrochem. Soc., 115, (1968), 933.
6. R. Benz, Z. Phys. Chem. N. F., 95, (1975), 25.

Figure 1. Double Electrochemical Cell Arrangement for the Determination of the Solubility and Diffusivity of Fluorine in Nickel.

Figure 2. Argon Gas Purification Train.

Figure 3. Experimental Setup for Electrochemical Measurement.

Figure 4. Experimental Cell for the Study of Electrode Polarizability.

Figure 5. Experimental Results of Electrode Polarization
Experiment at 850°C .

Figure 6. Experimental Results of Electrode Polarization Experiment at 900°C .

Figure 7. Experimental Results of Electrode Polarization Experiment at 950°C .

LEGEND

1 : Reference Electrode

2 : Electrolyte

Figure 8. Experimental Cell to Study the Fluorine Exchange Capacity of the Graphite Electrode.

LEGEND

1: Reference Electrode

2: Electrolyte

Figure 9. Experimental Cell to Study the Electrical Conductivity of Fluoride Compounds.

Figure 10. Experimental Setup for Fluorine Activity Probe.