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I am submitting herewith a dissertation written by Hsien-Lung Tsai entitled "Thermodynamic Study of Nickel-Molybdenum and Nickel-Chromium-Molybdenum Alloys by Using Solid Oxide Electrolytes." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgical Engineering.

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THERMODYNAMIC STUDY OF NICKEL-MOLYBDENUM AND
NICKEL-CHROMIUM-MOLYBDENUM ALLOYS BY
USING SOLID OXIDE ELECTROLYTES

A Dissertation
Presented for the
Doctor of Philosophy
Degree
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DEDICATION

To my wife, Chang-I, for her limitless faith, trust and perseverance.

To my sisters and brother, for their encouragement and undying love.

To my parents, for their boundless confidence and support throughout my educational career.

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I gratefully acknowledge the financial support provided through research grants by the United States Department of Energy.

Finally, I believe that all knowledge and wisdom comes from God (Col. 2:3). Consequently, I owe thanks to the Lord for giving me the physical strength, the mental faculties and opportunity to enjoy this accomplishment and the gratification that it has given me.

ABSTRACT

The thermodynamic properties of Mo and Cr have been determined in the f. c. c. phase region of Ni-Mo system and the Ni-corner of the Ni-Cr-Mo system, respectively. These properties are derived from the equilibrium electromotive force measurements using solid oxide electrolyte cells of the types: $\text{Mo, MoO}_2/\text{ThO}_2\text{-Y}_2\text{O}_3/\underline{\text{Mo}}$ (binary alloy), MoO_2 and $\text{Cr, Cr}_2\text{O}_3/\text{ThO}_2\text{-Y}_2\text{O}_3/\underline{\text{Cr}}$ (ternary alloy), Cr_2O_3 for Ni-Mo binary from 1123 to 1373 K and Ni-Cr-Mo ternary from 1173 to 1373 K, respectively.

In the f. c. c. phase region of Ni-Mo system, from 1123 to 1373 K, the Mo activity presents a positive deviation from ideality. The Mo activity decreases towards ideality as temperature increases.

In the f. c. c. phase region of Ni-Cr-Mo system, from 1173 to 1373 K, the Cr activity increases upon adding Mo into the Ni-Cr-Mo alloy. The Cr activity deviates negatively from ideality below five to ten atomic percent Cr and ten atomic percent Mo and positively above these compositions.

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CHAPTER I

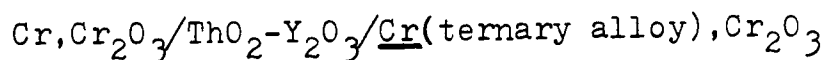
INTRODUCTION

There are various reasons to undertake the thermodynamic studies of binary and multicomponent systems. Thermodynamic data are required in order to formulate the conditions of phase equilibrium and provide the information of phases existing under stable, metastable or unstable condition. An example is the Ni-base superalloys, which have been extensively investigated in response to the demand for high-temperature materials of advanced high technology systems where the resistance to environmental degradation together with high temperature mechanical properties is required. Because undesirable phases may form, induce cracking, lead to low temperature failure, and to loss in rupture ductility, a deep understanding of the phase stability of the complex multi-phase, multi-component, Ni-base superalloy systems is necessary. Although it is difficult to measure all of the thermodynamic properties in complicated alloys like the Ni-base superalloys, it would be of great advantage to develop predictive methods which are physically well-grounded. The thermodynamic studies of unary, binary and ternary systems of Ni are very important to serve as a basis for development of physically well-founded predictive method consistent with the other well-known physical properties.

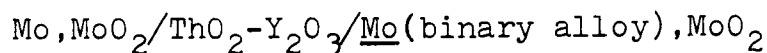
Furthermore, knowledge of accurate thermodynamic data has been required in order to achieve the successful computer coupling of phase diagrams and thermochemistry in the past two decades. To date, the solid electrolytic cell technique has been proven as an accurate, sensitive and easy technique for the measurement of thermodynamic data, especially for systems having very low oxygen chemical potential.

Among many ternary alloys whose thermodynamic properties are not accurately known, the nickel-chromium-molybdenum alloys within the face-centered cubic region were chosen for the present study because of their technical importance, as mentioned above. The accurate thermodynamic properties of chromium in these alloys have been determined between 1100 and 1373 K along three different fixed concentration lines in the nickel-corner (i.e. face-centered cubic region) of Ni-Cr-Mo system. The thermodynamic data of molybdenum in the Ni-Mo binary system, the bordering binary system of Ni-Cr-Mo alloy, have been also determined in this study in order to complete the evaluation of the thermodynamic properties of the nickel-corner of the Ni-Cr-Mo system.

These properties are derived from the equilibrium electromotive force measurements using solid oxide electrolyte cells of the types:



and



for Ni-Cr-Mo ternary system and Ni-Mo binary system,
respectively.

CHAPTER II

LITERATURE REVIEW

A. STANDARD FREE ENERGIES OF FORMATION OF MoO_2 AND Cr_2O_3

Galvanic cell applications in this study requires determining the oxygen potential of a two phase mixture of $\text{Mo}+\text{MoO}_2$ and $\text{Cr}+\text{Cr}_2\text{O}_3$ electrodes from the standard molar free energy of formation of MoO_2 and Cr_2O_3 which must be known over a wide range of high temperatures. These data have been previously obtained by various equilibrium methods including gas equilibration, calorimetry and electrochemical techniques.

Among the results from $\text{Cr}-\text{Cr}_2\text{O}_3$ measurements of the previous works (1-7), the data from Mazandarany and Pehlke's work (7) are the most reliable and lead to the following expression for the standard Gibbs free energy of formation of Cr_2O_3

$$\Delta G^\circ (\text{J/moleCr}_2\text{O}_3) = -1116,000 + 251.04T \quad (1150-1540 \text{ K}) \quad (1)$$

In their experimental study, electromotive force cells involving $\text{Cr}, \text{Cr}_2\text{O}_3$ electrodes and thoria-yttria electrolytes were used. They demonstrated the reversibility of these cells.

The expression of free energy of formation of MoO_2 :

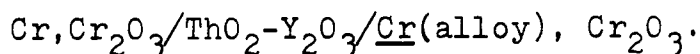
$$\Delta G^\circ (\text{J/moleMoO}_2) = -575,300 + 167.36 T \quad (2)$$

between 1020 and 1320 K was derived from the data of

e.m.f. measurement by Rapp (8). It is recommended to be the better data than the others obtained by various methods (9-20) because of the high accuracy of the solid oxide electrolyte technique used by Rapp in the e. m. f. measurement.

B. METAL ACTIVITIES OF Ni-Cr, Ni-Mo AND Ni-Cr-Mo SYSTEMS

The experimentally determined properties of Cr in solid Ni-Cr binary system have been studied by Mazandarany and Pehkle (21), using solid oxide electrolyte techniques with cells of the type:



Their chromium activities are shown in Figure 1. The results are more consistent with the nickel-chromium binary phase diagram proposed by Hansen (22) than those of the other investigations (4, 23, 24). Among various investigators there is reasonable agreement below 25 atomic percent chromium.

Figure 2 is the nickel-molybdenum partial phase diagram proposed by Guthrie and Stansbury (25) using x-ray and metallographic methods. The thermodynamics of nickel-molybdenum alloys has been investigated by Meshkov et al. (26) and Katayama et al. (27) with solid oxide electrolyte techniques. However, as shown in Figure 3, the activity from their e. m. f. measurements from 1073 to 1273 K for the alloys of less than 20 percent molybdenum conflict.

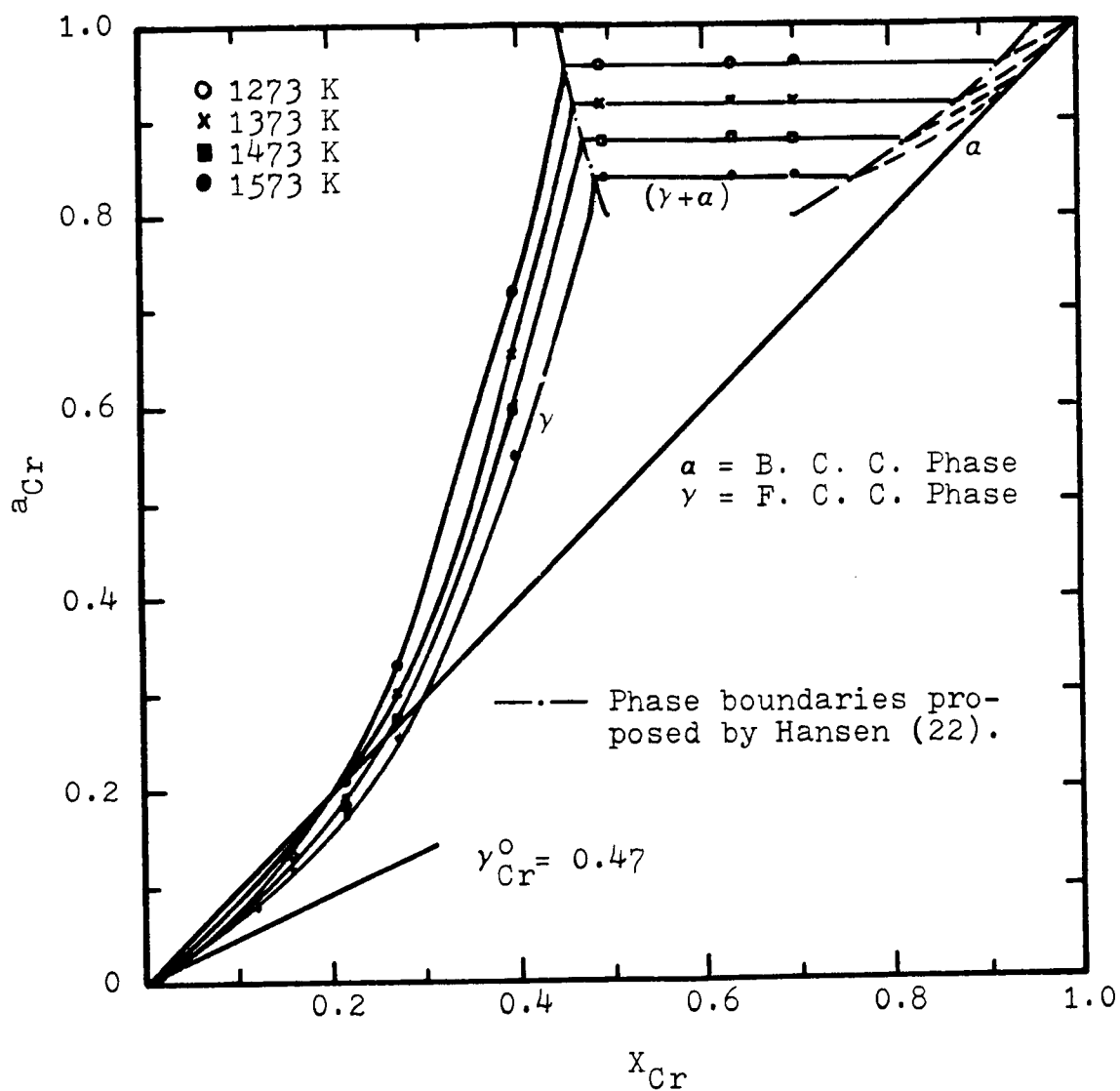


Figure 1. Thermodynamic activity of chromium in the solid Ni-Cr system referred to solid pure Cr (21).

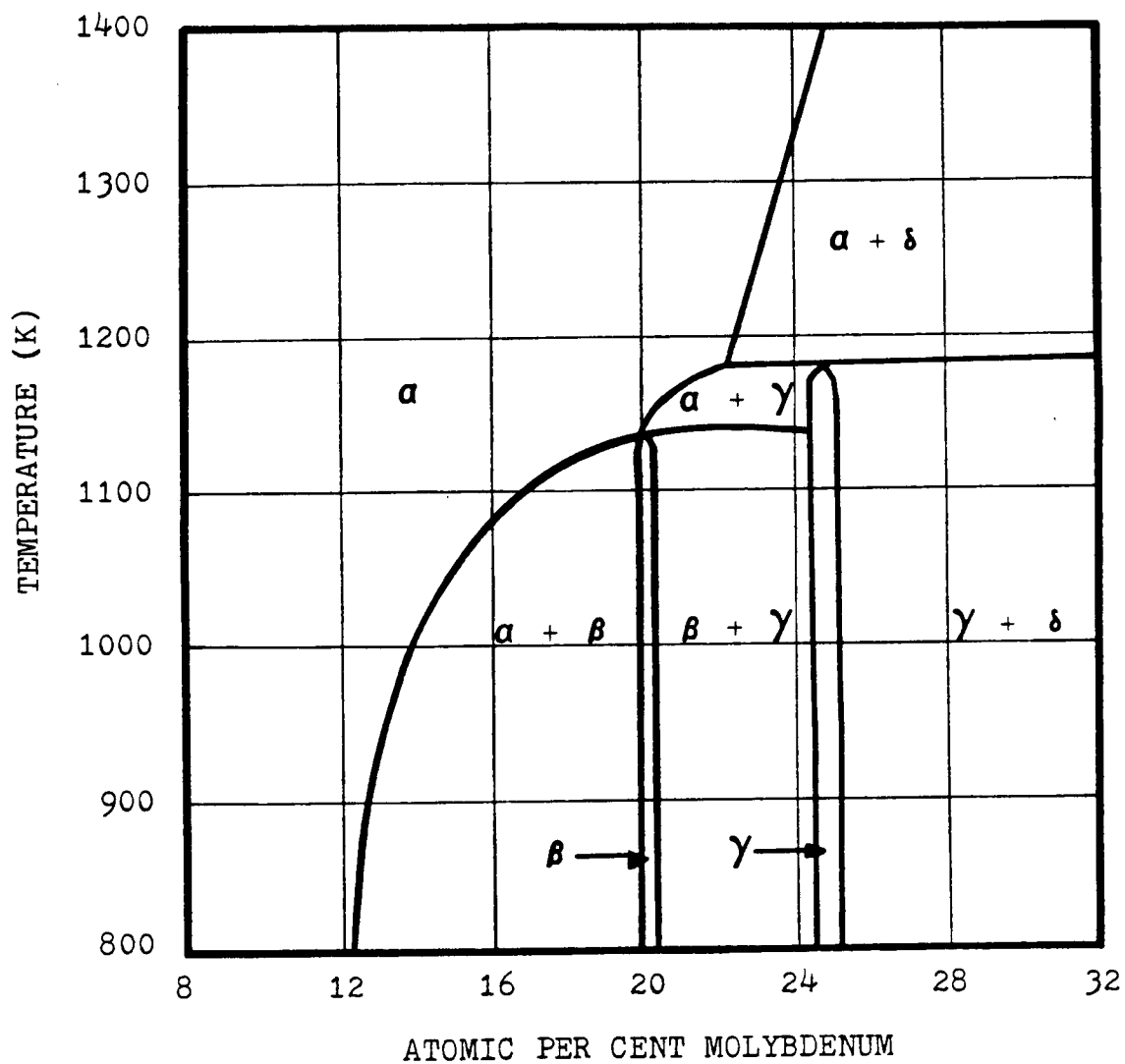


Figure 2. Partial Ni-Mo alloy phase diagram proposed by Guthrie (25).

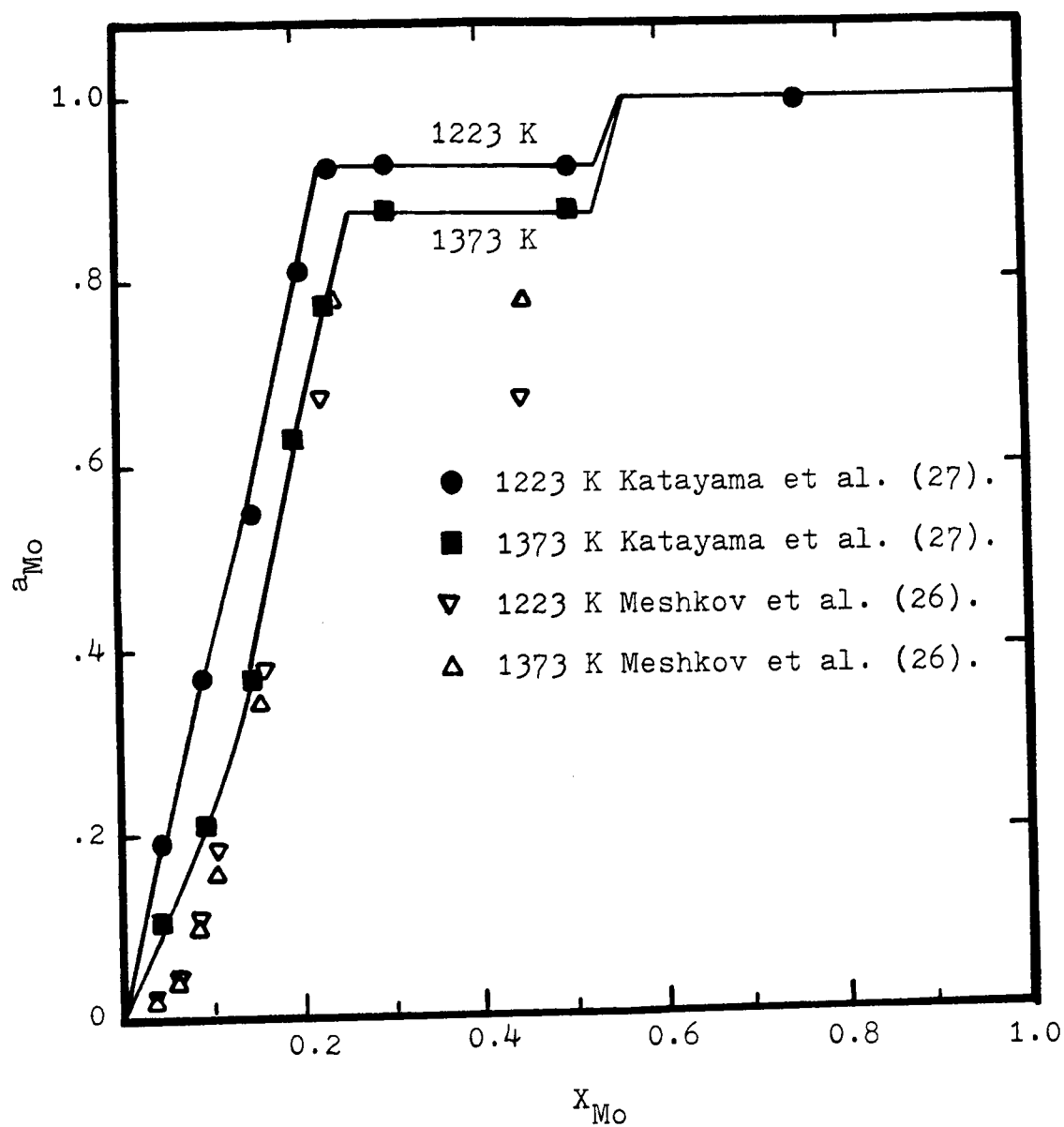


Figure 3. Thermodynamic activity of molybdenum in the solid Ni-Mo system referred to pure solid Mo (26,27).

Therefore, a similar technique was employed in the present study to establish the data of the nickel-molybdenum binary system over the temperature range 1173-1373 K. To date, there are no thermodynamic data of the nickel-chromium-molybdenum ternary alloys. Rideout et al. (28) and Bloom and Grant (29) published the isothermal phase diagram of nickel-chromium-molybdenum as shown in Figure 4. In this study the f. c. c. corner of nickel-chromium-molybdenum is selected because of its technical importance.

C. PERFORMANCE OF SOLID OXIDE ELECTROLYTES IN HIGH TEMPERATURE THERMODYNAMIC MEASUREMENT AND THE PRINCIPLES OF OPERATION

The solid oxide electrolyte technique employed in this study has been used intensively for high-temperature materials research after Kiukkola and Wagner published their papers (30, 31) in 1957. The experimental principles and performance of solid electrolyte in determining high-temperature thermodynamic data and rates of diffusion and chemical reactions have been summarized by numerous books and review articles (32-45).

Among over 30 solid electrolytes, the zirconia- and thoria-based solid solutions have been used successfully as electrolytes in high-temperature applications. Both solid solutions exhibit the fluorite crystal structure and have anionic Frenkel defect. The electrochemistry of the

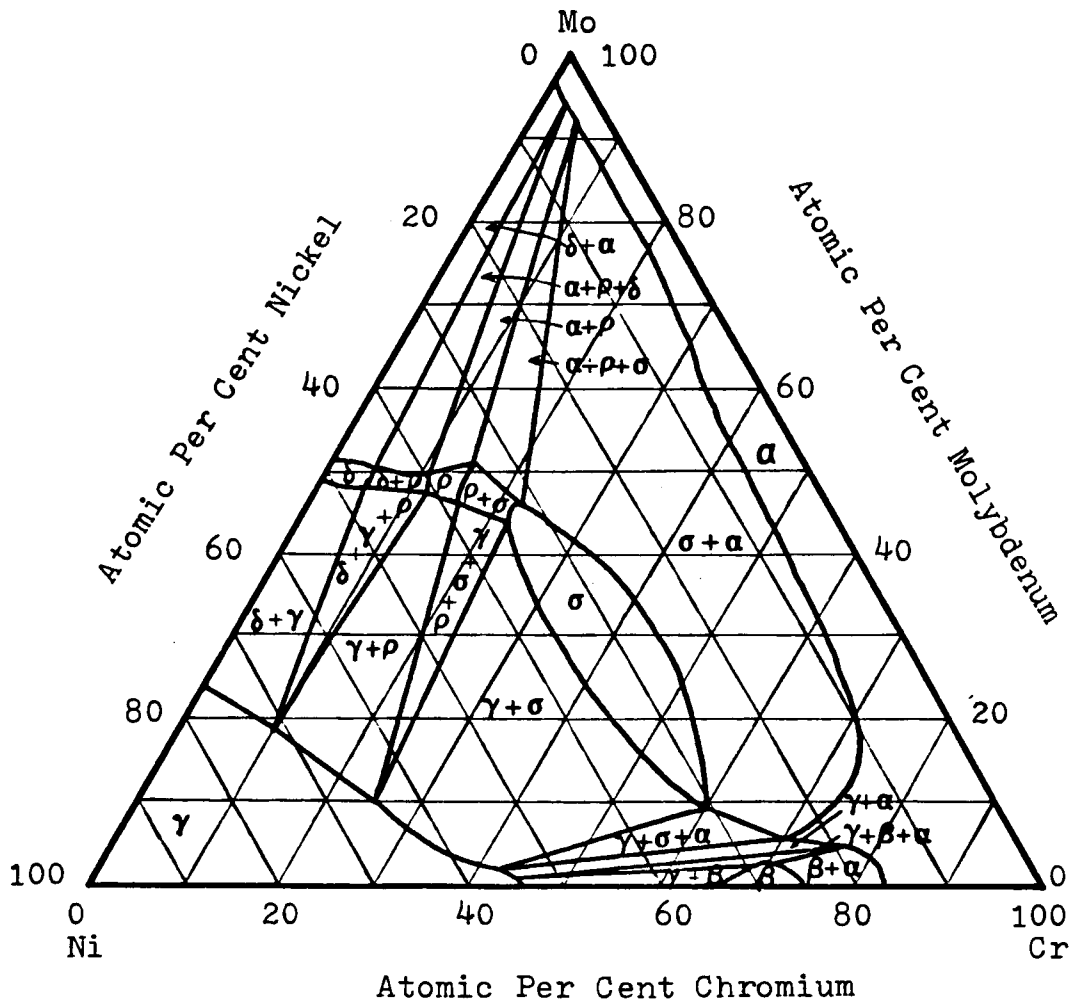


Figure 4. Isothermal section of the Ni-Cr-Mo phase diagram at 1523 K (29).

anionic Frenkel defect in these electrolytes is reviewed here first.

For example, in the thoria, a fully ionized and independent anionic, intrinsic Frenkel defect can be expressed in Kroger-Vink defect notation (46) as

$$O_O^X = V_O^{\cdot\cdot} + O_i^{\prime\prime} ; K_1 = [V_O^{\cdot\cdot}] [O_i^{\prime\prime}] . \quad (\text{EQ.1})$$

Here O_O^X represents oxygen on an anionic lattice site, $V_O^{\cdot\cdot}$ is an oxygen vacancy and $O_i^{\prime\prime}$ is an interstitial oxygen anion. All the notations used in this text are list in Table 1.

Under very high oxygen partial pressure, the predominant defects in thoria are electron holes, i.e. unoccupied electron sites in the valence band, and interstitial oxygen ions which can be expressed as

$$\frac{1}{2} O_{2(g)} = O_i^{\prime\prime} + 2 h^{\cdot} ; K_2 = [O_i^{\prime\prime}] [h^{\cdot}]^2 / p_{O_2}^{\frac{1}{2}} \quad (\text{EQ.2})$$

where $h^{\cdot}$ is an electron hole. Combination of the defect equilibrium with the electroneutrality condition,

$$[O_i^{\prime\prime}] = \frac{1}{2} [h^{\cdot}] ,$$

gives the electron hole concentration proportional to $p_{O_2}^{1/6}$.

Similarly, at very low oxygen partial pressure, oxygen vacancies and electrons are the predominant defects in the equilibrated thoria; thus

$$O_O^X = \frac{1}{2} O_{2(g)} + V_O^{\cdot\cdot} + 2 e^{\cdot} ; K_3 = [V_O^{\cdot\cdot}] [e^{\cdot}]^2 p_{O_2}^{\frac{1}{2}} \quad (\text{EQ.3})$$

and the electron concentration is proportional to $(p_{O_2})^{-1/6}$.

The predominant ionic defects are established between the high and low oxygen partial pressure regions where equation (1) is the predominant defect equation. Since the

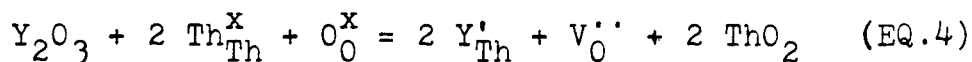
TABLE 1

NOTATIONS USED AND THEIR DEFINITIONS

Notation	Definition
O_O^X	Oxygen on an anionic lattice site; neutrally charged
$V_O^{\cdot\cdot}$	Doubly ionized oxygen vacancies; positively charged
$O_i^{\cdot\cdot}$	Doubly ionized oxygen interstitial; negatively charged
$e^{\cdot}$	Electrons; negatively charged
$h^{\cdot}$	Unoccupied electron site in the valence band (electron holes); positively charged
σ_e	Conductivity due to electrons
σ_h	Conductivity due to electron holes

oxygen partial pressure does not come into this equation anywhere, the ionic defect concentrations of vacancies or interstitials do not depend on oxygen partial pressure. A schematic representation of the variation of electrical conductivities for pure thoria with the oxygen partial pressure is shown in Figure 5.

The ionic defects can be greatly increased by doping. For example, the extrinsic defects are introduced by doping yttria into a thoria crystal. The ionic defect equation in the doped case may be written as



i.e. for every two yttrium ions added, one oxygen vacancy is formed to maintain electroneutrality in the solid solution. The higher the dopant concentration in the solid solution, the higher the oxygen vacancy concentration; therefore, the ionic conductivity dominates the electrical conductivity in this solid solution in a wider range of oxygen partial pressures than in pure thoria.

As shown in Figure 6, for thoria the ionic conductivity increases with the dopant concentration and reaches a maximum around eight mole percent Y_2O_3 (47, 48, 49). Because of the lattice distortion, defect interaction (46), vacancy clustering (50), or vacancy ordering (51), the ionic conductivity does not increase with dopant concentration above eight mole percent Y_2O_3 .

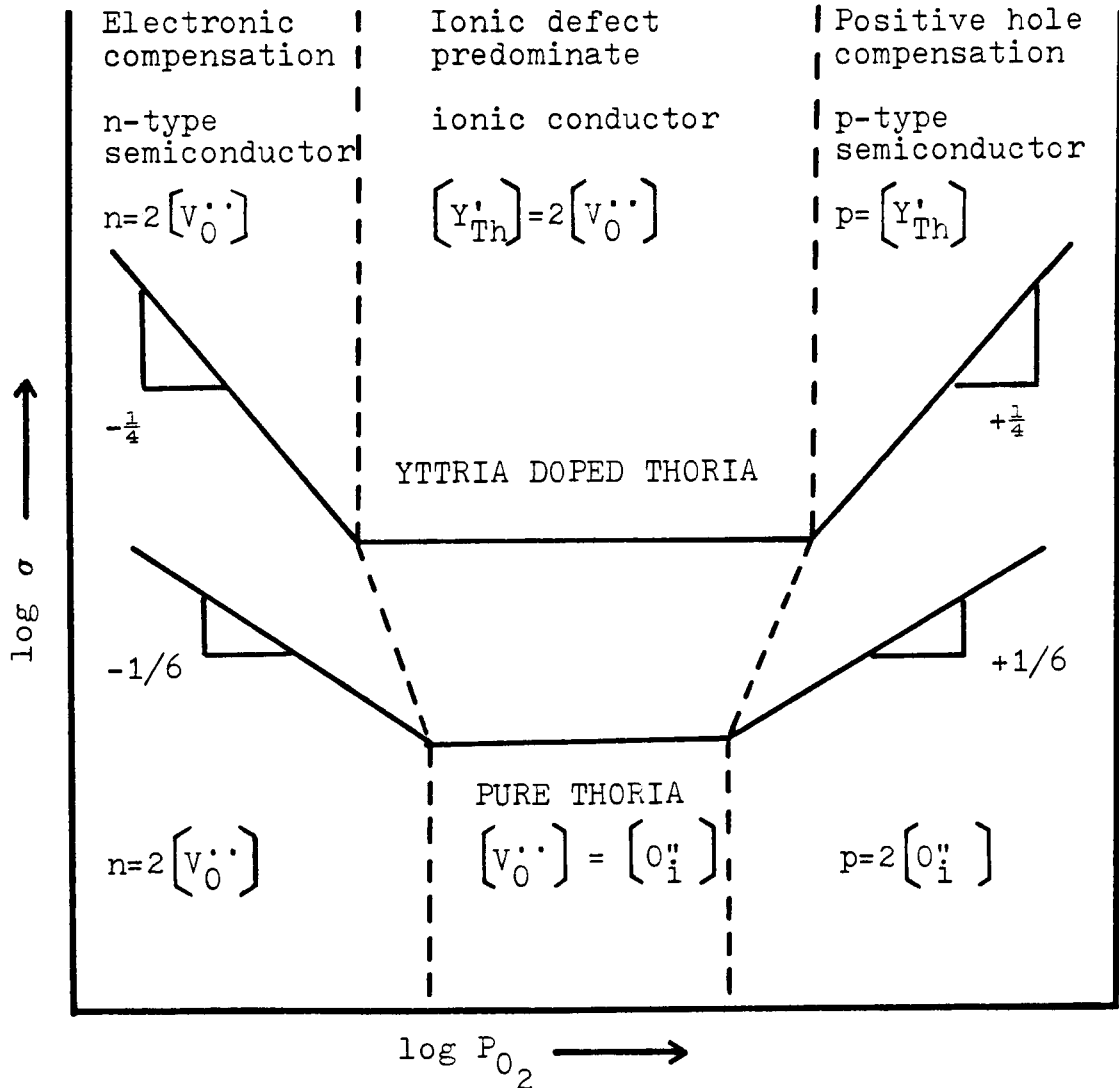


Figure 5. Schematic representation of the dependency of electrical conductivities for pure thoria and doped thoria on the oxygen pressure.

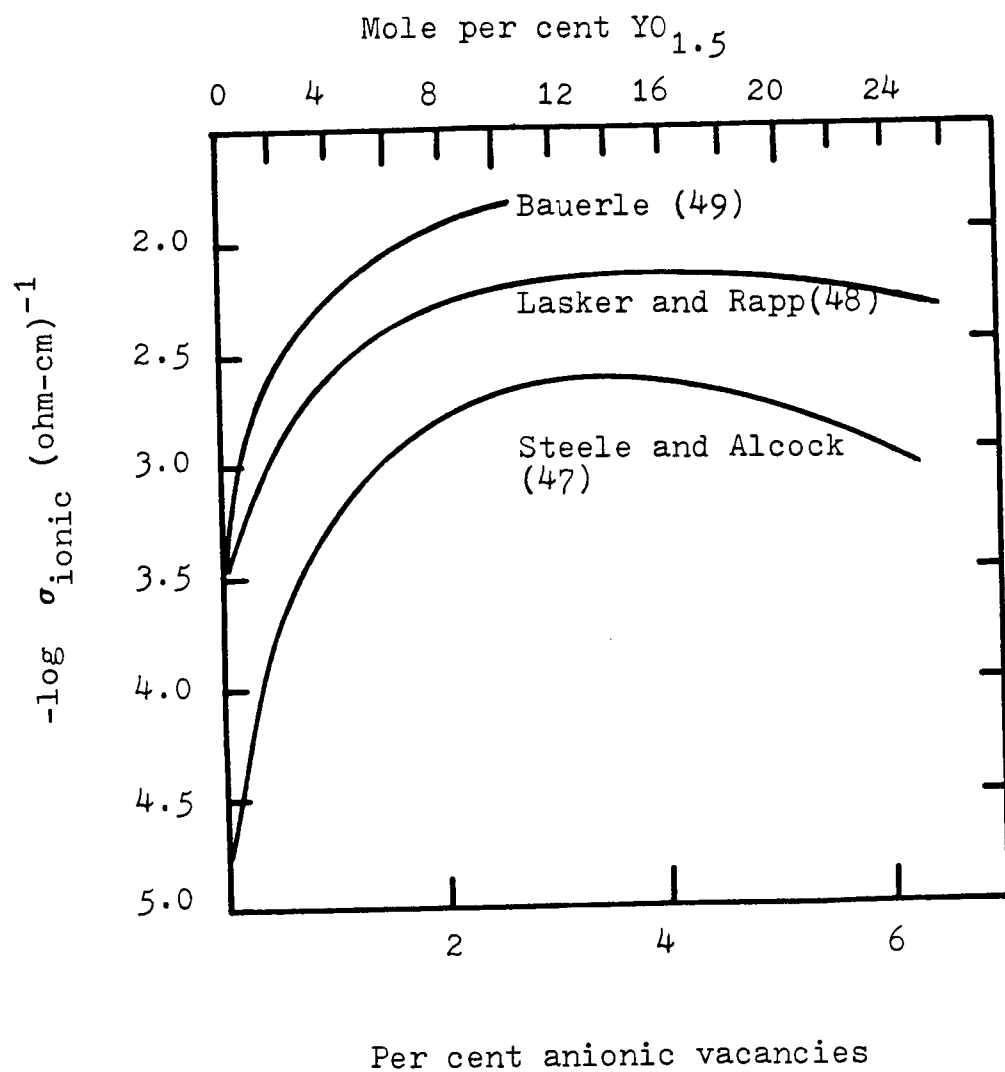


Figure 6. Ionic conductivity of $\text{ThO}_2(\text{Y}_2\text{O}_3)$ as a function of oxygen-vacancy concentration at 1273 K.

The dependence of the electrical conductivity of calcia-stabilized zirconia (CSZ) (52) and yttria doped thorium (YDT) (48) on oxygen partial pressure is shown in Figure 7. The p-type (electron hole type) electronic conductivity dominates at oxygen partial pressure above 10^{-6} atm in thorium solid solutions; in the CSZ electrolyte the predominant n-type (electron type) electronic conductivity exists at very low oxygen partial pressure (less than 10^{-22} atm).

The electrical conductivities of CSZ and YDT also depend on the temperature. Patterson (53) has estimated the electrolytic domain for various temperatures and oxygen partial pressures for CSZ and YDT electrolytes as shown in Figure 8. Inside the boundary lines more than 99 percent of the total conductivity is ionic. In other words, t_{ion} , the sum of anionic and cationic transference numbers, and also the ratio of ionic conductivity to total conductivity, equals unity inside the specific range of temperature and oxygen partial pressure. Since the ionic conductivity should be predominant for a compound to be a solid electrolyte, as shown later in this section, and the YDT meets this requirement at the experimental operation temperature and oxygen partial pressure of nickel-molybdenum binary and nickel-chromium-molybdenum ternary systems, the YDT was selected as the electrolyte of the electromotive force cell for the activities measurement in this study.

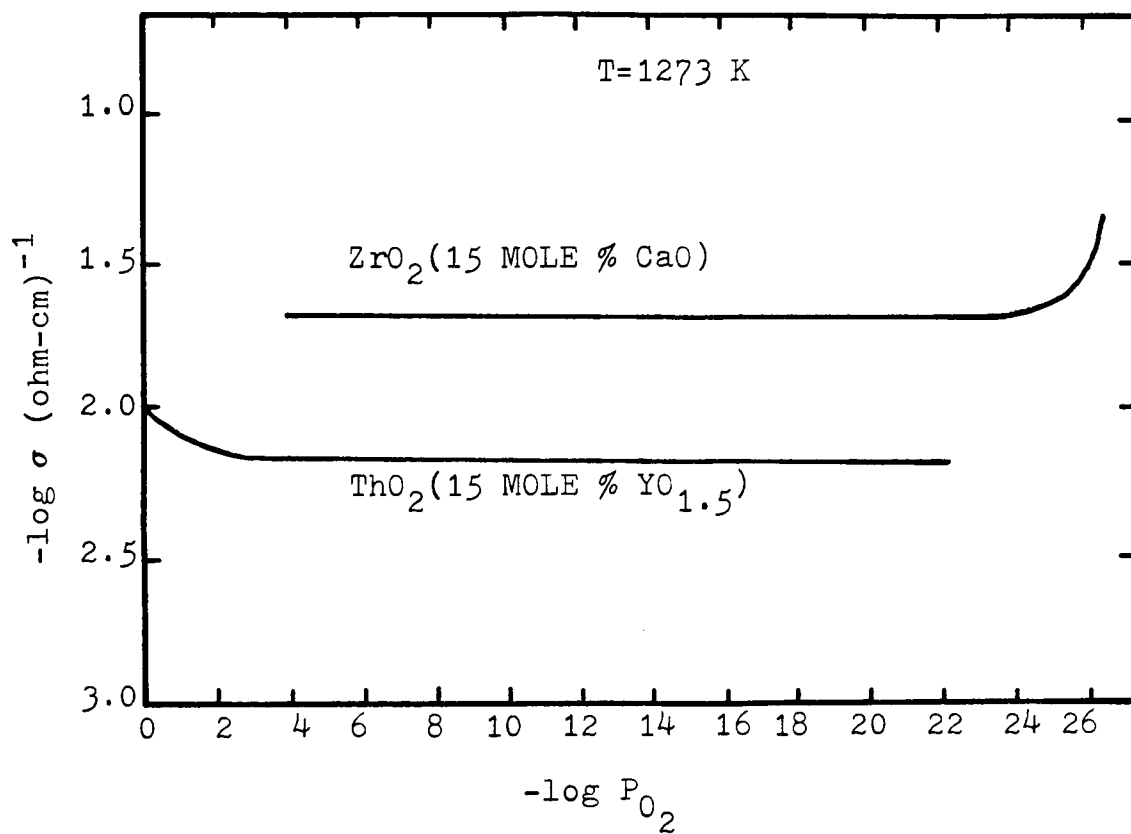


Figure 7. Electrical conductivity of ZrO₂(CaO) (52) and ThO₂(Y₂O₃) (48) as a function of oxygen partial pressure.

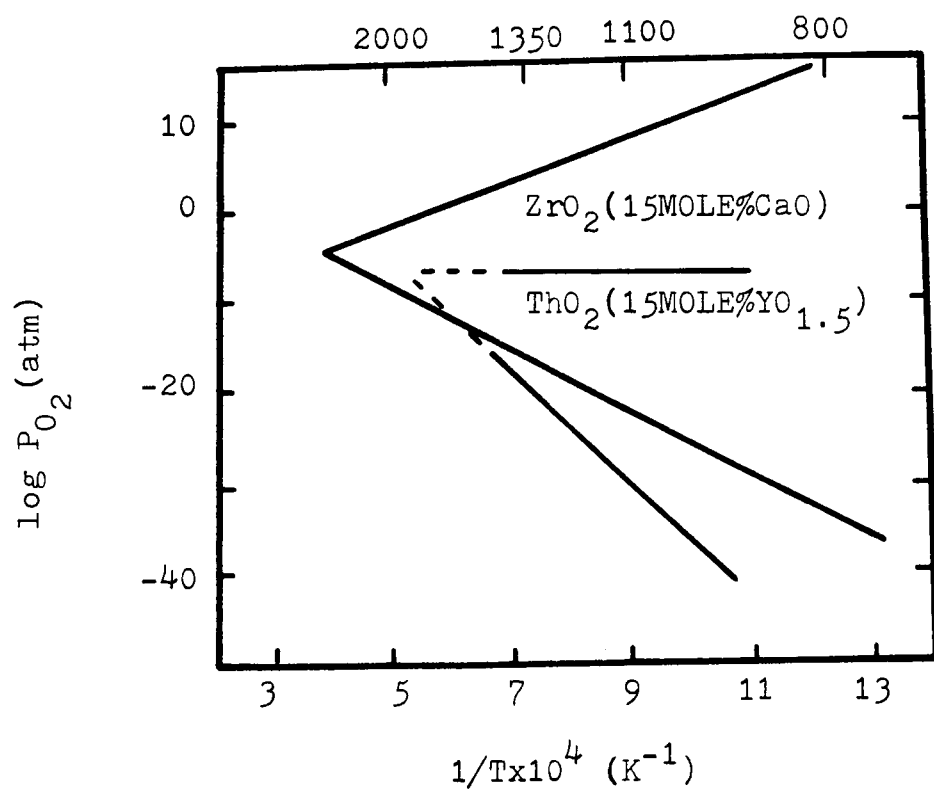


Figure 8. Electrolytic domain for CSZ and YDT (53).

Wagner (54) has shown that the electromotive force (E) of an electrochemical cell is related to the chemical potential drop of species X across the electrolyte of no diffusion potentials by

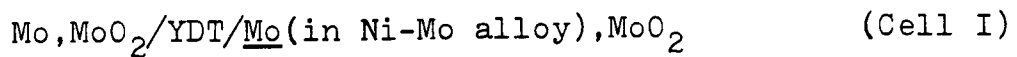
$$E = \frac{-1}{n F} \int_{\mu_X''}^{\mu_X'} t_{ion} d \mu_X \quad (EQ.5)$$

where n is absolute magnitude of charge on ionic carriers; F is Faraday's constant; μ_X' , μ_X'' are chemical potentials of X at the left- and right-hand electrode-electrolyte interfaces, respectively; and t_{ion} is the transport number of the ions. In the case $t_{ion}=1$, the equation becomes

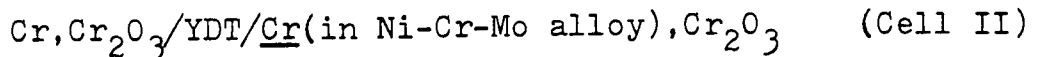
$$\Delta \mu = -n E F. \quad (EQ.6)$$

Then the open circuit cell voltage (E) indicates the free energy change between two electrodes in this cell.

The electrodes used in this study were solid multi-phase coexistence electrodes. They require an internal equilibration between the two components in the electrode as well as an equilibration between the electrode and the electrolyte, and may be written:



and



with the virtual chemical reaction



in nickel-molybdenum binary system for cell I and



in nickel-chromium-molybdenum ternary system for cell II.

The unknown activity of metal in the right-hand electrode can be obtained by the equation

$$\Delta \bar{G}_M = \Delta \mu_X = -nFE = RT \ln a_M \quad (\text{EQ.9})$$

with the $\text{Cr}+\text{Cr}_2\text{O}_3$ and $\text{Mo}+\text{MoO}_2$ electrodes of the defined and very well-known oxygen potentials used as the reference electrodes.

However, there are some limitations in the use of solid oxide electrochemical cells for the equilibrium measurement at high temperature (44, 45). First of all is the electronic conduction in the electrolyte if the electrolyte contains the improper dopant and becomes a semiconductor (e. g. tantalum (V) cation doped in thoria) or the equilibrium oxygen partial pressure of the electrode is higher or lower than the electrolytic domain of the selected electrolyte. Then the measured voltages are less than their actual values, this is, the measured activities will be overestimated. Using high purity electrolytes over a temperature and oxygen partial pressure range within the electrolytic domain improves this problem. Secondly, the migration of molecular oxygen through the porosity of micro-cracks in the electrolyte from one electrode to other changes the oxygen chemical potentials at the two electrode-electrolyte interfaces. This problem can be solved by proper sample preparation and sintering techniques and careful operation of the electrochemical cell. Other problems such as undesirable chemical reactions, deviations

from equilibrium among electrode constituents and the influence of the gaseous phase can cause difficulties in maintaining a fixed chemical potential in the electrode-electrolyte interface.

CHAPTER III

EXPERIMENTAL PROCEDURE

A. MATERIALS PREPARATION

Yttria-Doped Thoria Electrolyte

Thorium nitrate, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (99.99%), from SPEX Industrial Inc. and yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%), from Alfa were the starting materials to produce the yttria doped thoria electrolyte. The nitrates were mixed in the proportions of 8.29 parts of thorium nitrate to one part of yttrium nitrate by weight to prepare the desired composition of thoria- eight mole percent yttria solid solution. The nitrate mixtures were then dissolved in distilled water. Two techniques were then available to make the oxides.

The first method was the dehydration of the nitrate solution. The nitrate solution was dehydrated at about 400 K, leaving a salt-like material at the bottom of the beaker. The material was transferred into an alumina boat and heated in air at about 650 K to removed the remainder of nitric oxide. The powder then was ground carefully in order to obtain a homogeneous solid solution after subsequent sintering.

The other method was the filtration and dehydration of the oxalate precipitate suggested by Subbarao et al. (56). The nitrate solution was placed in an ice bath and stirred vigorously while saturated oxalic acid was added drop by

drop. Thorium and yttrium oxalate salts were precipitated. The oxalate precipitate was filtered and washed until the precipitate was free of acids. The precipitate was dehydrated at about 400 K and then calcined at 1200 K for eight to twelve hours. Some investigators (56,57) recommend the oxalate-precipitate as the most satisfactory starting material to produce the dense oxide electrolyte pellets. However, the oxide powder product by the first method proved an excellent way to make an excellent electrolyte in our laboratory for this study.

After either technique, the resulting homogeneous and fine grained oxide powder was ground to less than 325 mesh and pressed into pellets 12.7mm (1/2 inch) in diameter and four to eight mm (0.157 to 0.315 inch) thick at a pressure about 14 Kg/mm^2 (20,000 psi). Green pellets were heated in air at about 1000 K for one day to remove the traces of nitric oxide in the pellets. The pellets were then sintered in a vacuum of 10^{-8} atm at 2200 to 2500 K for seven hours in a covered stabilized zirconia or thoria crucible with loose thoria powder as packing material to prevent the pellets from sticking to each other and contact with undesirable vapor species from the tantalum heating element and molybdenum heat shields during sintering in the bee-hive furnace. The x-ray fluorescence analysis of the pellets after sintering in the scanning electron microscope showed slight molybdenum contamination, but which did not affect

their performance in this study, as discussed in a following section (p.35). However, the tantalum contamination should be avoided in any case; for example, the sintering temperature should be as low as possible to avoid the vaporization of tantalum and high enough to achieve high density of the pellets. Longer holding time at sintering temperature also provides the chance for the tantalum contamination. The heating and cooling rate during sintering were less than 100 K per hour in order to avoid cracking in the pellets. The lattice parameters of the pellets after sintering were determined by x-ray diffraction. The compositions of the pellets were derived by the linear interpolation of the lattice parameters of pure thoria and ten mole percent Y_2O_3 doped thoria as 5.60 Å and 5.56 Å, respectively (56). The density was pycnometrically observed to be above 99.9% of the theoretical density. An yttria-doped thoria electrolyte pellet made by Das (58) of 6.625 mole percent Y_2O_3 with 99.96% of the theoretical density was also used in this study. As a necessary condition for a good electrolyte, the pellets were ivory white to transparent. The pellets were polished on a polymer plate with six micron diamond paste before use in a cell.

Reference Electrodes

The molybdenum-molybdenum oxide reference electrodes were prepared by pre-reducing the molybdenum (VI) oxide to molybdenum (IV) oxide under prepurified hydrogen atmosphere

at about 800 K for four days before mixing with the molybdenum powder in about one to five volume ratio. The molybdenum powder was from Cerac and about two micron average particle size, oxide-reduced, 99.9 percent pure. The molybdenum (VI) oxide was from Cerac and with a particle size less than 100 mesh and 99.9 percent pure.

The mixed powder was pressed at about 42 Kg/mm^2 (60,000 psi) into pellets 9.53 mm (0.375 inch) in diameter and eight mm (0.315 inch) thick, and heated in a dry argon atmosphere for one day at 1300 K. X-ray analysis to one percent accuracy of the resulting mixture was used to check that the mixture consists of only molybdenum and molybdenum (IV) oxide. The sintered pellets were polished finally on a hard plastic plate with nine micron diamond paste before use in a cell.

The chromium oxide reference electrodes were prepared by mixing high purity chromium powder (-325 mesh size and 99.99 percent pure from Cerac) with 99.8 percent pure chromium (III) oxide (-5 micron size from Cerac) in a ten to one weight ratio, and pressing at about 42 Kg/mm^2 (60,000 psi) into pellets 9.53 mm (0.375 inch) in diameter and eight mm (0.315 inch) thick. The pellets were sintered in a four percent hydrogen-argon atmosphere for a week at 1500 K. The sintered pellets were polished on a hard plastic plate with nine micron diamond paste before use in a cell.

Ni-Mo and Ni-Cr-Mo Alloys and Their Alloy Electrodes

The nickel-molybdenum and nickel-chromium-molybdenum alloys of desired compositions were produced by melting mixture of the high purity elements to give the alloys in Table 2. The chemical analysis of the nickel pellets with average five mm size is listed in Table 3. The 99.97 percent pure molybdenum rod with 6.5 mm diameter was from Alfa Products. The average size of highly pure chromium chips was five mm square and two mm thick. Over ten grams of the elements for each alloy were weighed and placed in an arc furnace and melted at least ten times for each side of the alloy ingots under argon atmosphere. The weight loss during the melting process was less than 0.1 percent for each alloy. The alloys were then heat-treated for two days at 1500-1600 K in hydrogen to allow homogenization. X-ray diffraction analysis and the optical microscope were used for the examination of alloy composition and homogenization.

All the alloys were filed by alumina wheel on a hand grinder to produce relatively fine particles for subsequent pelletizing. In some case, the iron or iron oxide was found in the alloy powder after the grinding process. So a magnet was used to remove the iron or iron oxide from the alloy powder. The alloy powders were then mixed with about one half the volume of molybdenum (IV) oxide or chromium (III) oxide to produce the nickel-molybdenum or nickel-chromium-molybdenum alloy electrodes, respectively. The mixtures

TABLE 2

THE NOMINAL COMPOSITIONS OF Ni-Mo AND Ni-Cr-Mo
ALLOYS USED IN THIS RESEARCH

Designation	Mo Content		Cr Content		Ni Content
	At.%	Wt.%	At.%	Wt.%	
Ni-Mo alloys					
Ni-5Mo	5.0	7.9			bal
Ni-12Mo	12.0	18.2			bal
Ni-17Mo	17.0	25.1			bal
Ni-20Mo	20.0	29.0			bal
Ni-Cr-Mo alloys					
Ni-3.8Cr-19.7Mo	19.7	28.3	3.8	3.0	bal
Ni-4.8Cr-19.2Mo	19.2	28.1	4.8	3.8	bal
Ni-5Cr-7.6Mo	7.6	11.9	5.0	4.3	bal
Ni-10Cr-7.2Mo	7.2	11.4	10.0	8.6	bal
Ni-10Cr-10.8Mo	10.8	16.7	10.0	8.4	bal
Ni-10Cr-14.4Mo	14.4	21.8	10.0	8.2	bal
Ni-20Cr-9.6Mo	9.6	15.1	20.0	17.1	bal
Ni-20Cr-12.8Mo	12.8	19.8	20.0	16.7	bal

TABLE 3

CHEMICAL ANALYSIS OF Ni PELLETS

Element	Content (p.p.m. by weight)
C	-50.0
Co	- 0.2
Cu	- 1.0
Fe	-20.0
O ₂	50.0
S	2.0
Al	- 1.0
Mn	- 1.0
Si	- 1.0
Sn	- 1.0
Ni	bal
Others	- 0.5 ea.

were pressed at about 70 Kg/mm^2 (100,000 psi) into the pellets of 6.35 mm (0.25 inch) diameter and eight mm (0.312 inch) thickness. It is very important to pre-sinter the alloy electrodes before introduction into the cell in order to pre-equilibrate the electrode components and assure equal oxygen potential throughout. The nickel-molybdenum alloy electrodes were sintered under purified argon at about 1300 K for one day, while the nickel-chromium-molybdenum alloy electrodes were sintered in bee-hive furnace with a 10^{-4} torr vacuum at 1500 K for twelve hours. The molybdenum dioxide powder used for these alloy electrodes were the same as that used in the reference electrodes.

B. EMF CELL ARRANGEMENT, EXPERIMENTAL APPARATUS AND CELL GEOMETRY

The emf cell arrangement used in this study is shown schematically in Figure 9. Two separate chambers were employed in this study to minimize oxygen transport in the gas phase from one electrode to another. The yttria-doped thoria electrolyte was placed in the outer chamber between the reference electrode and an alumina tube in which the alloy electrode was placed. An alumina push rod in the inner chamber as well as the compression spring at both the alumina tubes pressed the three pellets together. A platinum O-ring was placed between the electrolyte and the alumina tube to improve the separation of gas from each chamber to other chamber.

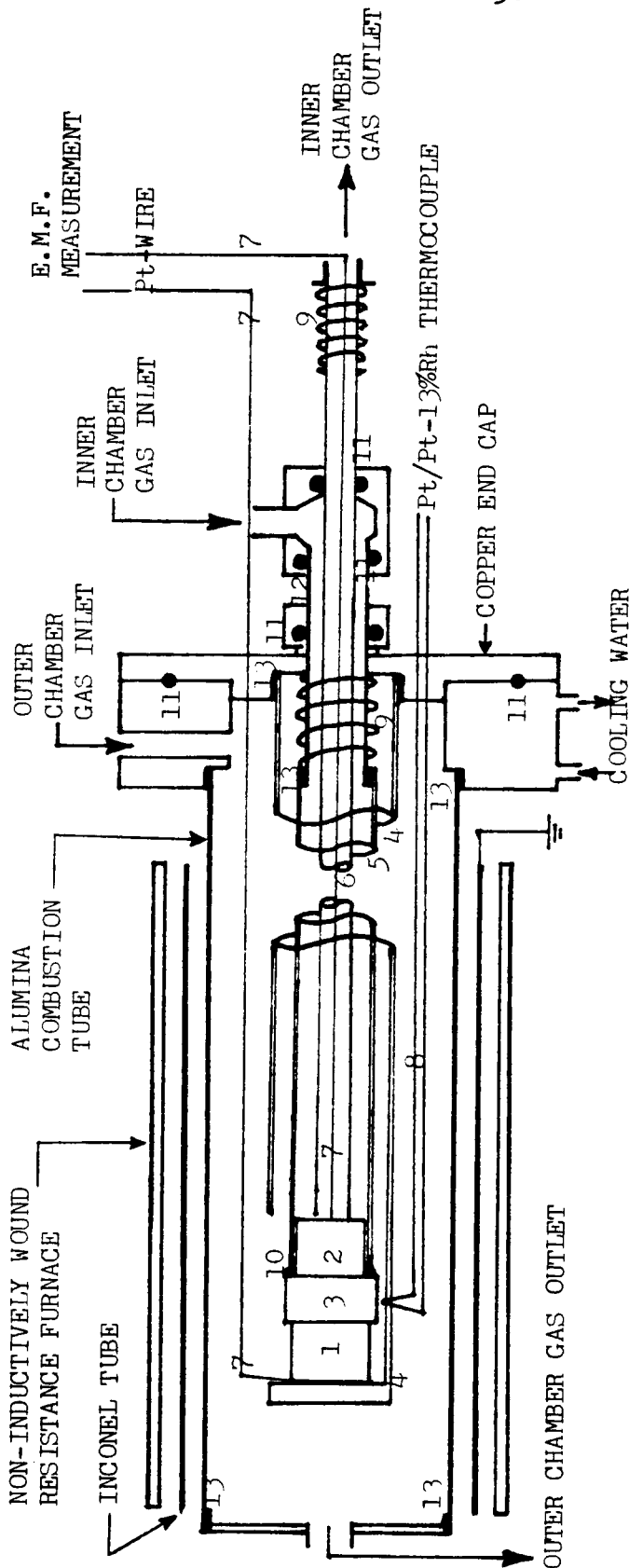


Figure 9. Schematic drawing of cell arrangement.

1. reference electrode;
2. alloy electrode;
3. electrolyte;
4. alumina tube;
5. alumina tube for the inner chamber;
6. alumina push tube;
7. Pt-wire;
8. Pt/Pt-13%Rh thermocouple;
9. compression spring;
10. Pt O-ring;
11. O-ring;
12. copper tube;
13. ceramic-copper epoxy joint.

The cell voltages were measured by connecting two 0.254 mm (0.010 inch) diameter platinum leads from each electrode to a high accuracy (± 0.005 percent of input ± 5 uv) DC differential voltmeter (Fluke Model 895A) which was calibrated on May 12, 1980. The temperature of the emf cells was measured by a platinum-13 percent rhodium/platinum thermocouple placed next to the electrolyte of the emf cell using a digital multimeter (Data Precision 3500) with an accuracy of ± 0.004 percent of reading ± 10 uv. An electrically grounded Inconel tube surrounding the alumina tube minimized induced voltages from a non-inductively wound resistance furnace, as well as to broaden the hot zone (± 1 K) to about one and a half inch at 1373 K and to increase its heat capacity to reduce temperature fluctuations. A proportioning controller unit with a platinum-13 percent rhodium/platinum thermocouple placed near the furnace windings was used to control the furnace temperature to better than ± 0.5 K over any run.

C. PROCEDURES FOR EQUILIBRIUM EMF CELL MEASUREMENT

The assembled cell was placed in the hot zone of the furnace. Before the furnace power was turned on, both the chambers were evacuated and tested for gas tightness. After the system reached twenty micron of vacuum, the furnace power was turned on to degas the cell assembly and the ceramic materials of the chambers. The purified argon was introduced to both the chambers after the temperature of the

furnace increased to about 600 K. The high purity grade argon (minimum purity 99.995 percent) was purified before entering the cell chambers by passing over BASF Catalyst R 3-11 (approx. 30 percent copper in highly dispensed form stabilized on a carrier, activated by various additional components), anhydrous phosphorus pentoxide and ascarite.

The cell was heated to the highest temperature, 1373 K, for the initial equilibration and allowed to achieve thermodynamic equilibrium over two to three days. After a steady voltage at the highest temperature was obtained, the furnace temperature was decreased by 50 K and the cell was allowed to equilibrate at the new temperature until a new steady voltage was obtained. This procedure was repeated by either increasing or decreasing the furnace temperature until all the equilibrium voltages were measured at least twice at every 50 K interval over the temperature range 1073-1373 K. A typical run usually continued for a couple of weeks, even one month, before shutting off the furnace power to terminate the run.

To demonstrate the reversibility of the apparently stable voltage in the cells, a small d.c. current was passed across the cell leads for a short time (about fifteen seconds) and the cell voltage returned to the original value within ± 1 mv after overnight re-equilibration. The same result was obtained by passing the current in the opposite direction.

D. EXPERIMENTAL PRECAUTIONS AND UNCERTAINTIES

To demonstrate the reliability of the experimental apparatus, a "check" cell involving two reference electrodes in the suitable oxygen partial pressure range, $\text{FeO}+\text{Fe}_3\text{O}_4$ and $\text{Mo}+\text{MoO}_2$, was used first at the beginning of these emf measurement experiments. The experimental apparatus was re-designed several times and the electrolyte was replaced by an improved one, then the check cell duplicated the known voltage. The re-design included the change of the cell geometry from common gas compartment to double gas compartments and the conversion of all connection tubes to glass with high vacuum stopcock, copper and stainless steel flexure tubes.

The electrolyte made by oxide process, by which the electrolyte is made directly from their oxide powder by cold pressing and sintering, was shown unsuitable for the equilibrium emf measurement after several test runs. The technique to prepare the electrolyte has been improved in the author's laboratory as described in a previous section.

The contact surfaces of electrodes and electrolyte were polished carefully to make a near perfect contact, or otherwise, the emf reading would be unstable when the flow rate of argon changed.

some alloy and reference electrodes were examined by x-ray diffraction and by x-ray fluorescence analysis in the scanning electron microscope before and after use in a cell

to check if any side reactions occurred. In some alloy electrodes iron was detected, probably picked up during the grinding process or original existence in the metal oxide powder. After sintering for a very long period, say, one week, the iron oxide was reduced and replaced the molybdenum and chromium in the nickel-chromium-molybdenum alloy and led to a false measurement of the activities of chromium.

The measured equilibrium voltages were reliable because they met the condition that all the equilibrium voltages obtained from such a stepwise cooling and heating procedure were self-consistent. Also the independently duplicated runs for an alloy were carried out to verify the reliability of the emf measurement.

A group of measured values from repeated equilibrium voltage measurements of a cell can be expressed by a mean value and the standard deviation which describes the distribution of the measurements about the mean. In this study, a one millivolt uncertainty in the cell voltage corresponds to about 400 joules uncertainty in ΔG° by the equation

$$\delta(\Delta G^\circ) = -nF(\delta E).$$

CHAPTER IV

RESULTS AND DISCUSSION

A. EXPERIMENTAL VERIFICATION OF THE E.M.F. MEASUREMENTS

The voltage of the "check" cell $\text{FeO}, \text{Fe}_3\text{O}_4/\text{YDT}/\text{Mo}, \text{MoO}_2$ was measured first. The results, shown in Figure 10, demonstrate the reliability of the improved experimental apparatus and the YDT electrolyte over the temperature range from 1150 to 1373 K in this study.

The high degree of reversibility in the measured emf for the cells of Ni-Mo and Ni-Cr-Mo system was indicated by a highly reproducible emf for various temperature cycling and duplicate runs and a high linearity of the emf-temperature lines obtained by the method of least squares. Table 4 gives an example for the comparison of results from duplicate runs by using two apparatus for a Ni-Cr-Mo alloy with low chromium and molybdenum contents. Even though the emf showed ± 2 mv deviation at some temperatures, the derived activities of chromium in this test alloy are essentially identical in each run.

To verify the reversibility of the alloy electrodes, the emf of the cell $\text{Ni-5Cr-7.6Mo}, \text{Cr}_2\text{O}_3/\text{YDT}/\text{Ni-10Cr-14.4Mo}, \text{Cr}_2\text{O}_3$ was measured and then compared with that calculated by the difference of the measured emf's of the two cells, $\text{Ni-5Cr-7.6Mo}, \text{Cr}_2\text{O}_3/\text{YDT}/\text{Cr}, \text{Cr}_2\text{O}_3$ and $\text{Ni-10Cr-14.4Mo},$

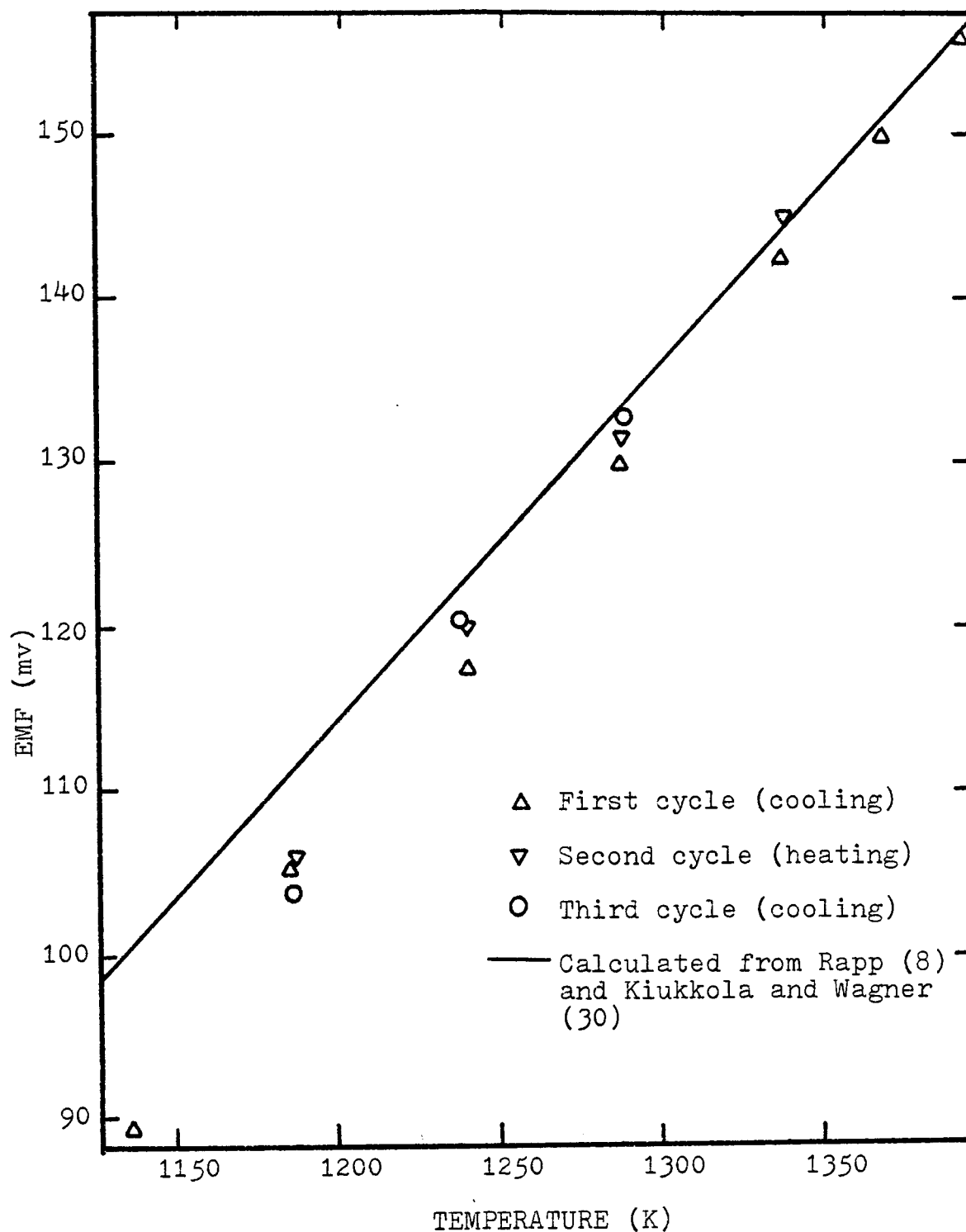


Figure 10. Experimental and calculated data for the cell:
 $\text{FeO}, \text{Fe}_3\text{O}_4 / \text{YDT} / \text{Mo}, \text{MoO}_2$.

TABLE 4

COMPARISON OF RESULTS FROM TWO INDEPENDENT
RUNS FOR A TEST Ni-Cr-Mo ALLOY

Temperature (K)	E(mv)		Activity of Cr	
	Run 47	Run 54	Run 47	Run 54
1248	185.8	186.4	0.006	0.006
1275	189.8	189.5	0.006	0.006
1340	200.4	204.6	0.005	0.005
1370	206.6	209.8	0.005	0.005

$\text{Cr}_2\text{O}_3/\text{YDT}/\text{Cr},\text{Cr}_2\text{O}_3$. As shown in Table 5, the calculated and measured emf's agree within the experimental deviation (± 0.8 mv or ± 0.4 mv for each cell).

B. CALCULATIONS OF THE THERMODYNAMIC PROPERTIES FROM THE EXPERIMENTAL RESULTS

Once the reliable voltages E were measured for each cell containing an alloy electrode at every 50 K interval over the temperature range 1073 to 1373 K, the method of least squares was employed to obtain a linear voltage-temperature relation. The activities of molybdenum and chromium for each temperature were derived from the equations

$$-4FE = RT \ln a_{\text{Mo}} \quad (\text{EQ.10})$$

and

$$-3FE = RT \ln a_{\text{Cr}} \quad (\text{EQ.11})$$

respectively.

The partial molar free energy of molybdenum in Ni-Mo alloys and chromium in Ni-Cr-Mo alloys was obtained by the equations

$$\Delta \bar{G}_{\text{Mo}}(X_{\text{Mo}}, T) = \Delta \mu_{\text{Mo}}(X_{\text{Mo}}, T) = -4FE(X_{\text{Mo}}, T) \quad (\text{EQ.12})$$

and

$$\Delta \bar{G}_{\text{Cr}}(X_{\text{Cr}}, X_{\text{Mo}}, T) = \Delta \mu_{\text{Cr}}(X_{\text{Cr}}, X_{\text{Mo}}, T) = -3FE(X_{\text{Cr}}, X_{\text{Mo}}, T) \quad (\text{EQ.13})$$

where X is the mole fraction of Mo or Cr in alloys and $F=96.49$ joule per millivolt-mole. Also the partial molar

TABLE 5

COMPARISON OF MEASURED AND CALCULATED EMF FOR THE CELL
 $\text{Ni-5Cr-7.6Mo, Cr}_2\text{O}_3/\text{YDT}/\text{Ni-10Cr-14.4Mo, Cr}_2\text{O}_3$
 AT 1373 K

Cell	E(mv) s*
Ni-5Cr-7.6Mo, Cr_2O_3 /YDT/Cr, Cr_2O_3 ; measured	142.74 0.44
Ni-10Cr-14.4Mo, Cr_2O_3 /YDT/Cr, Cr_2O_3 ; measured	85.39 0.24
Ni-5Cr-7.6Mo, Cr_2O_3 /YDT/Ni-10Cr-14.4Mo, Cr_2O_3 ; calculated from above	57.35 0.68
Ni-5Cr-7.6Mo, Cr_2O_3 /YDT/Ni-10Cr-14.4Mo, Cr_2O_3 ; measured	56.8

*s: standard deviation

entropies and enthalpies of formation of the alloys for molybdenum and chromium were obtained by the equations

$$\Delta \bar{S}_{\text{Mo}}(X_{\text{Mo}}) = 4F \left(-\frac{dE(X_{\text{Mo}}, T)}{dT} \right)_{X_{\text{Mo}}}, \quad (\text{EQ.14})$$

$$\Delta \bar{H}_{\text{Mo}}(X_{\text{Mo}}) = 4F \left[T \left(-\frac{dE(X_{\text{Mo}}, T)}{dT} \right)_{X_{\text{Mo}}} - E(X_{\text{Mo}}, T) \right], \quad (\text{EQ.15})$$

$$\Delta \bar{S}_{\text{Cr}}(X_{\text{Cr}}, X_{\text{Mo}}) = 3F \left(-\frac{dE(X_{\text{Cr}}, X_{\text{Mo}}, T)}{dT} \right)_{X_{\text{Cr}}, X_{\text{Mo}}}, \quad (\text{EQ.16})$$

and

$$\Delta \bar{H}_{\text{Cr}}(X_{\text{Cr}}, X_{\text{Mo}}) = 3F \left[T \left(-\frac{dE(X_{\text{Cr}}, X_{\text{Mo}}, T)}{dT} \right)_{X_{\text{Cr}}, X_{\text{Mo}}} - E(X_{\text{Cr}}, X_{\text{Mo}}, T) \right]. \quad (\text{EQ.17})$$

The excess partial free energy for molybdenum and chromium is also given by

$$\Delta \bar{G}_{\text{Mo}}^{\text{xs}} = RT \ln \gamma_{\text{Mo}} \quad (\text{EQ.18})$$

and

$$\Delta \bar{G}_{\text{Cr}}^{\text{xs}} = RT \ln \gamma_{\text{Cr}} \quad (\text{EQ.19})$$

where γ_{Mo} and γ_{Cr} are the activity coefficients of molybdenum and chromium, respectively, which may be defined as the ratio of the activity to the mole fraction.

C. Ni-Mo SYSTEM

The experimental data are plotted in Figure 11. The method of least squares was employed to obtain the emf-temperature line over the temperature range 1150 to 1373 K for each cell. The least squares analyses of the experimental data are summarized in Table 6. The dashed line in Figure 11 indicates that due to the unstable emf in the cell for a

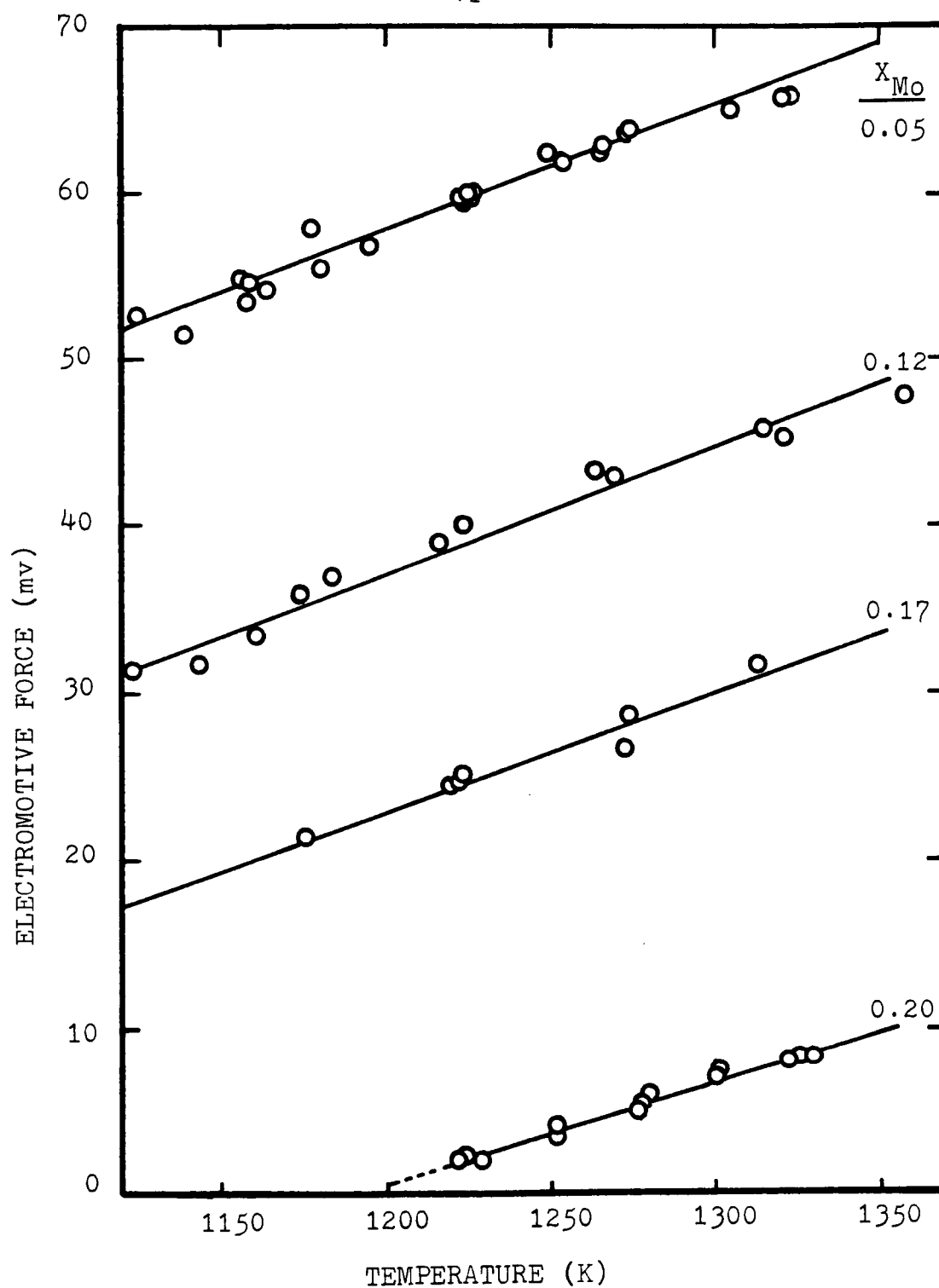


Figure 11. Experimental data for cell: Mo,MoO₂/YDT/Ni-Mo alloy,MoO₂.

TABLE 6

LEAST SQUARES ANALYSES OF THE EXPERIMENTAL
DATA FOR SOLID Ni-Mo ALLOYS

X_{Mo}	$E \pm s^*$ (mv)	$\Delta \bar{G}_{\text{Mo}}$ (Joule/mole)	Temperature range (K)
0.05	$-30.7 + 0.074T \pm 0.8$	11,800-28.6T	1125-1323
0.12	$-51.4 + 0.074T \pm 0.9$	19,800-28.6T	1123-1358
0.17	$-61.2 + 0.070T \pm 0.8$	23,600-27.0T	1176-1313
0.20	$-72.8 + 0.061T \pm 0.3$	28,100-23.6T	1223-1328

*s: standard deviation

very long period of time no measurements were made in that temperature range. The derived thermodynamic properties of molybdenum in solid nickel-molybdenum alloys are listed in Table 7. Figure 12 shows the positive deviation of the molybdenum activity from ideality in the nickel-rich single phase region of the nickel-molybdenum binary system. The activity approached ideality as temperature increases. Reliable equilibrium emf data in the alloy with 22.5 atomic percent molybdenum were difficult to obtain because the phase boundary of alpha and delta phases fall around the maximum working temperature of the furnace, 1400 K (see Figure 2).

Figure 13 compares of the activity of molybdenum in the nickel-rich single phase of the nickel-molybdenum binary system of this study to that reported by Katayama et al. (27) and Meshkov et al. (26). In Katayama's work, the calcia-stabilized zirconia was used as the electrolyte in cells with a common gas compartment. In this case, an equilibrium emf reading is usually affected by both the exposure of electrodes under the same argon stream and the imperfect contact of the electrodes with electrolyte. The slightly high activity of molybdenum obtained by Katayama et al. and the slightly low activity of molybdenum in the study of Meshkov et al. by using yttria-doped thoria electrolyte in the cell with a separate gas compartment may be due to the difficulty of the achievement of equilibrated oxygen

TABLE 7

THERMODYNAMIC PROPERTIES OF Mo IN SOLID Ni-Mo ALLOYS
DERIVED DIRECTLY FROM CELL POTENTIALS*

X_{Mo}	T (K)	E (mv)	a_{Mo}	γ_{Mo}	$-\Delta\bar{G}_{\text{Mo}}$ (J/mol)	$\Delta\bar{G}_{\text{Mo}}^{\text{xs}}$ (J/mol)
0.05	1150	54.09	0.113	2.253	20,876	7,766
	1250	61.47	0.102	2.040	23,725	7,409
	1350	68.84	0.094	1.875	26,569	7,055
0.12	1150	33.62	0.257	2.145	12,976	7,296
	1250	41.01	0.218	1.817	15,828	6,207
	1350	48.41	0.189	1.577	18,684	5,114
0.17	1150	19.50	0.455	2.677	7,526	9,416
	1250	26.51	0.374	2.198	10,232	8,183
	1350	33.53	0.316	1.857	12,941	6,947
0.20	1250	3.75	0.870	4.350	1,447	15,279
	1350	9.87	0.712	3.561	3,809	14,255

* All properties based on a reference state of oxygen-saturated pure solid Mo.

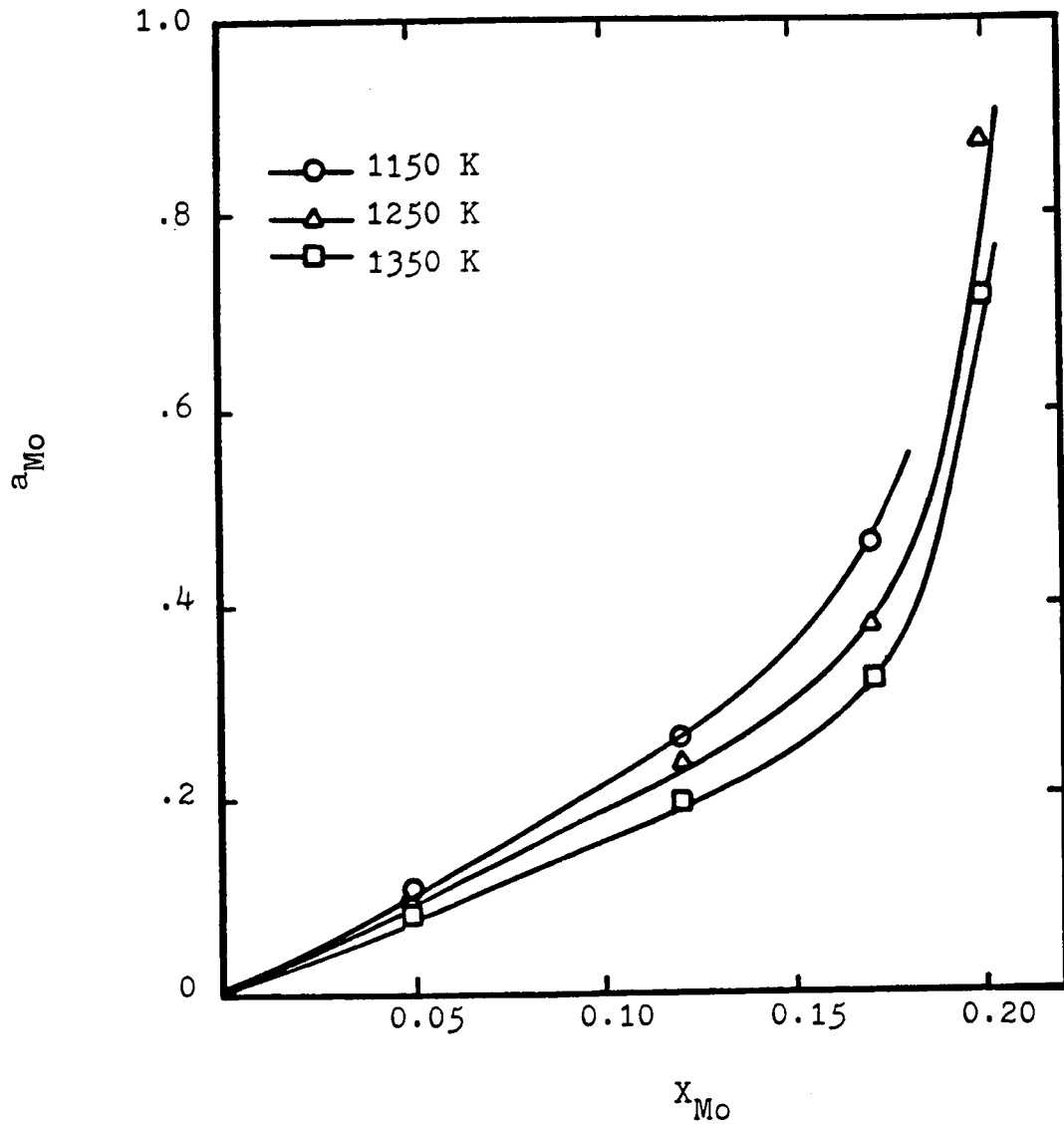


Figure 12. Molybdenum activity in the Ni-rich single phase region of the Ni-Mo binary system. The data are from the least squares analyses of the experimental data.

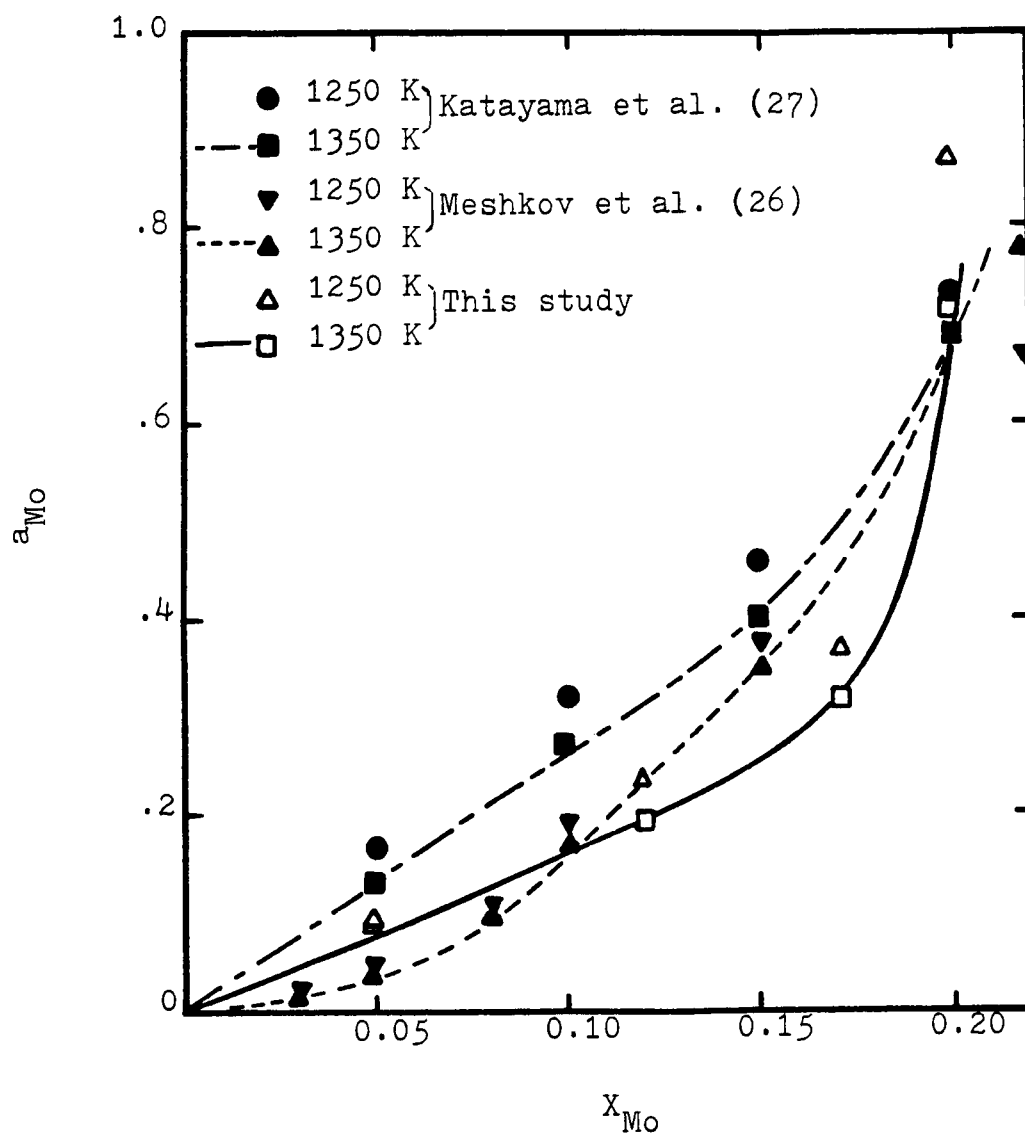


Figure 13. Comparison of the activity of molybdenum in the Ni-rich single phase region of Ni-Mo binary system as reported by various investigations.

potential over all of the molybdenum-molybdenum dioxide electrode. The cause of this difficulty may perhaps be attributed to the excess oxygen potential in the molybdenum-molybdenum dioxide pellets. The excess oxygen forms a thin blocking layer of molybdenum dioxide at the electrode-electrolyte interface. In several test runs of this study, a very thin black layer was observed at the electrode-electrolyte interface and was very easy to polish off by six micron diamond paste. The problem was solved by removing the excess oxygen from the original molybdenum powder by pre-annealing in pure hydrogen at about 800 K and reducing the metal-metal oxide ratio to five to one.

The molybdenum penetration through the electrolyte by grain boundary diffusion, as has been assumed (12), can not be proved since the trace of molybdenum was equally distributed in the electrolyte during the previous sintering process. However, no cation grain boundary diffusion thru the electrolyte was concluded by the indirect evidence of that no chromium was detected by x-ray fluorescence in scanning electron microscope in the cross section of electrolyte after extensive use in the nickel-chromium-molybdenum alloy cells. All electrolytes had the same shiny surface after extensive use in the emf measurement in this study.

The thermodynamic data for the nickel-molybdenum system over the temperature range of 600 to 1100 K can be

calculated by applying the heat capacity data of the nickel-molybdenum binary system to the equation

$$\Delta G_T = \Delta G_{T_1} + \int_{T_1}^T \Delta C_p dT - T \int_{T_1}^T \frac{\Delta C_p}{T} dT \quad (\text{EQ. 20})$$

where ΔG_{T_1} is the free energy of formation of the nickel-molybdenum alloy at temperature T_1 (between 1100 and 1373 K) obtained by emf measurement. In Figure 14 are shown the heat capacities of a Ni-20 atomic percent Mo alloy, pure nickel and pure molybdenum from 600 to 1300 K as reported by Norem (59), Stansbury et al. (60), Meschter et al. (61) and Choudhury and Brooks (62), respectively. Table 8 summarizes the free energy of formation of Ni-20 atomic percent Mo alloy at temperature between 650 and 1350 K obtained by the Equation 20.

D. Ni-Cr-Mo SYSTEM

Figure 15 shows the plots of experimental data for each alloy. The least squares analyses of the experimental data are summarized in Table 9. The activities of chromium in the solid nickel-chromium-molybdenum system referred to solid pure chromium are shown in Figure 16. The thermodynamic properties of chromium in solid nickel-chromium-molybdenum alloys derived directly from cell potential on a reference state of oxygen-saturated solid pure chromium are summarized in Table 10.

Within the temperature region of this study, the $\Delta \bar{H}$ and $\Delta \bar{S}$ terms are assumed constant with temperature. Therefore,

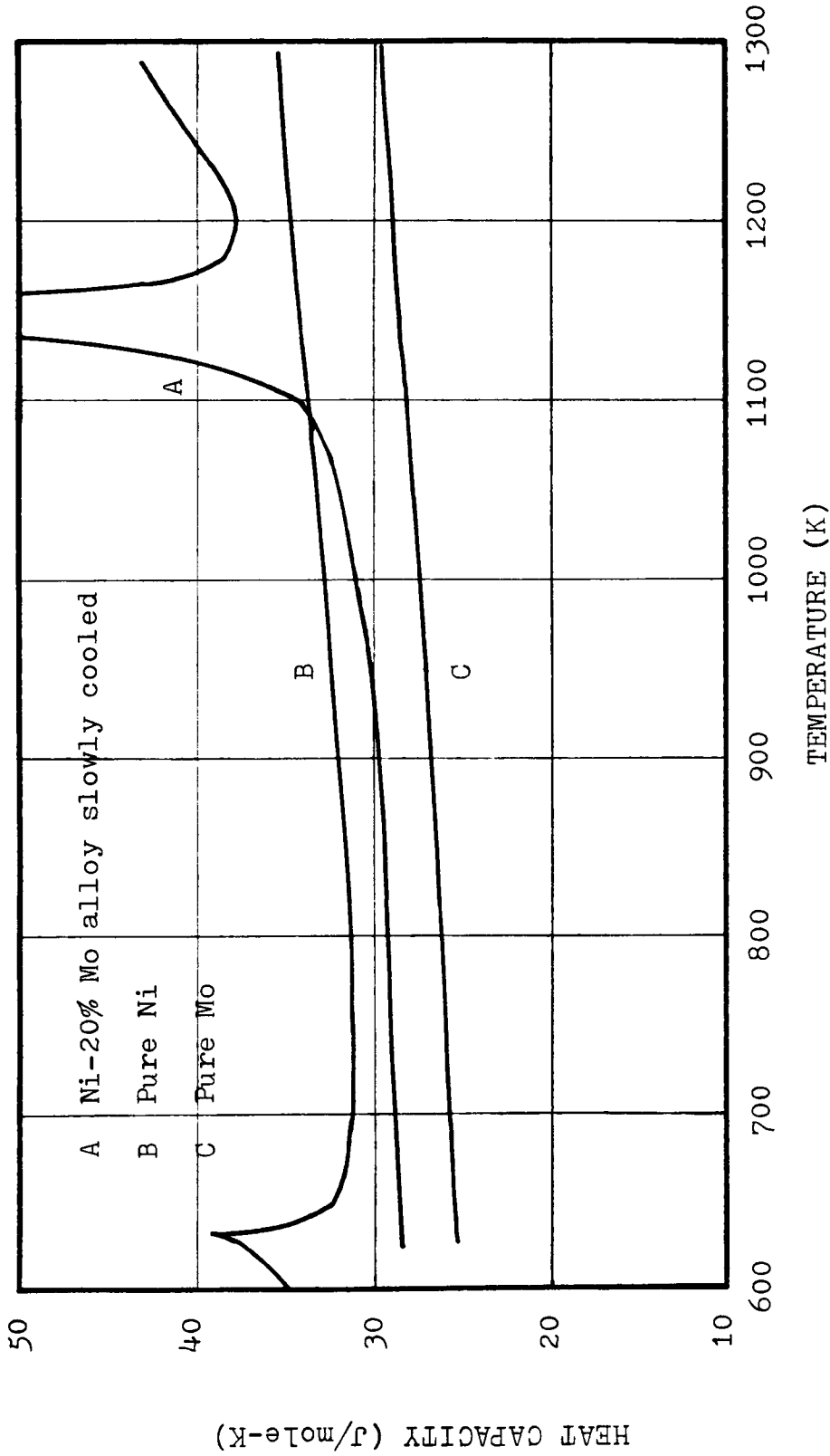


Figure 14. The heat capacities of a Ni-20 atomic percent Mo alloy (59), pure Ni (60,61) and pure Mo (62) from 600 to 1300 K.

TABLE 8

THE FREE ENERGY OF FORMATION OF A Ni-20Mo ALLOY AT
TEMPERATURES BETWEEN 650 AND 1350 K

Temperature (K)	ΔG (J/mole)
650	-3,705
750	-3,794
850	-3,773
950	-3,773
1050	-3,539
1150	-3,345
1250	-3,588
1350	-4,161

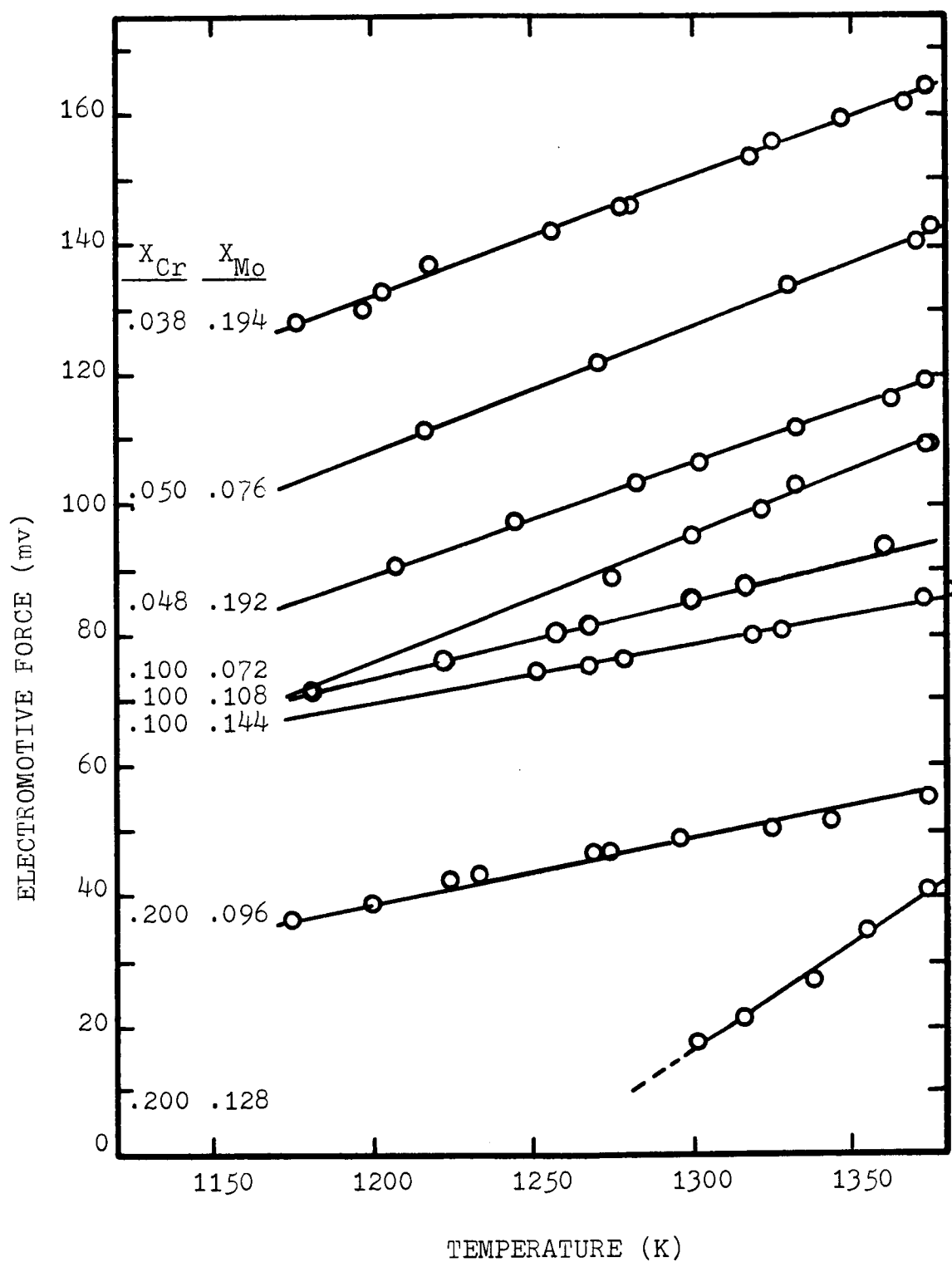


Figure 15. Experimental data for cell: $Cr, Cr_2O_3/YDT/Ni-Cr-Mo$ alloy, Cr_2O_3 .

TABLE 9

LEAST SQUARES ANALYSES OF THE EXPERIMENTAL DATA
FOR SOLID Ni-Cr-Mo ALLOYS

X_{Cr}	X_{Mo}	$E \pm s^*$ (mv)	$\Delta \bar{G}_{Cr}$ (J/mole)	Temperature range (K)
0.038	0.194	$-86.9 + 0.182T$ ± 0.7	$25,100 - 52.8T$	1176-1373
0.050	0.076	$-122.1 + 0.192T$ ± 0.4	$35,400 - 55.7T$	1216-1374
0.048	0.192	$-108.4 + 0.165T$ ± 0.6	$31,400 - 47.8T$	1207-1373
0.100	0.072	$-153.8 + 0.192T$ ± 0.8	$44,500 - 55.6T$	1274-1376
0.100	0.108	$-72.2 + 0.122T$ ± 0.3	$20,900 - 35.2T$	1182-1360
0.100	0.144	$-37.8 + 0.090T$ ± 0.2	$10,900 - 25.9T$	1251-1383
0.200	0.096	$-79.5 + 0.098T$ ± 0.9	$23,000 - 28.5T$	1130-1373
0.200	0.128	$-427.9 + 0.341T$ ± 0.5	$123,800 - 98.8T$	1291-1374

* s: standard deviation

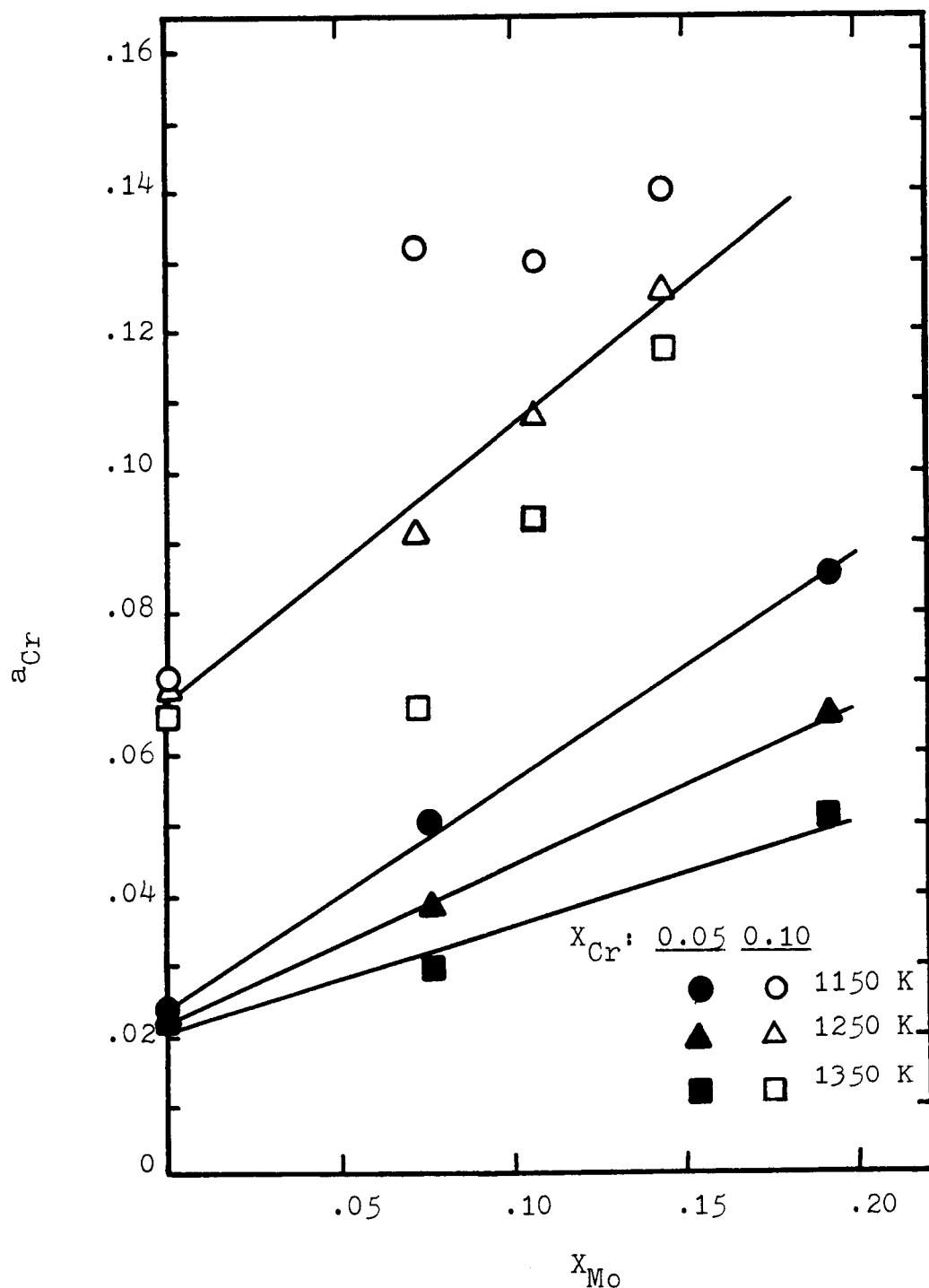


Figure 16. Thermodynamic activity of chromium in the solid Ni-Cr-Mo system referred to pure solid Cr. The data at $X_{Mo} = 0$ are from Mazandarany and Pehlke (21). The others are from the least squares analyses of the experimental data.

TABLE 10

THERMODYNAMIC PROPERTIES OF Cr IN SOLID Ni-Cr-Mo ALLOYS
DERIVED DIRECTLY FROM CELL POTENTIALS*

X_{Cr}	X_{Mo}	T (K)	E (mv)	a_{Cr}	γ_{Cr}	$-\Delta\bar{G}_{Cr}$ (J/mole)	$\Delta\bar{G}_{Cr}^{xs}$ (J/mole)
0.038	0.194	1150	122.95	0.024	0.636	35,589	-4,323
		1250	141.19	0.020	0.516	40,869	-6,884
		1350	159.43	0.016	0.431	46,149	-9,445
0.050	0.076	1150	98.67	0.050	1.009	28,561	81
		1250	117.87	0.038	0.750	34,119	-2,986
		1350	137.07	0.029	0.583	39,696	-6,053
0.048	0.192	1150	81.38	0.085	1.702	23,556	5,086
		1250	97.88	0.065	1.309	28,332	2,801
		1350	114.79	0.052	1.036	33,227	397
0.100	0.072	1150	66.96	0.132	1.317	19,382	2,633
		1250	86.16	0.091	0.907	24,940	-1,010
		1350	105.36	0.066	0.661	30,498	-4,654
0.100	0.108	1150	67.67	0.129	1.289	19,588	2,427
		1250	79.83	0.108	1.082	23,108	819
		1350	92.00	0.093	0.932	26,631	-787
0.100	0.144	1150	65.28	0.139	1.386	18,896	3,119
		1250	74.24	0.126	1.265	21,490	2,440
		1350	83.20	0.117	1.170	24,083	1,761
0.200	0.096	1150	33.82	0.359	1.796	9,790	5,598
		1250	43.67	0.296	1.482	12,641	4,085
		1350	53.52	0.252	1.258	15,492	2,572
0.200	0.128	1300	15.94	0.653	3.263	4,614	12,781
		1350	32.97	0.427	2.136	9,544	8,521

* All properties based on a reference state of oxygen-saturated pure solid Cr.

the intercept and slope of the linear equation of $\Delta\bar{G}$ versus temperature represent the $\Delta\bar{H}$ and $\Delta\bar{S}$, respectively.

The emf equilibrium measurements for the nickel-chromium binary system reported by Mazandarany and Pehlke (21) (see Figure 1) indicated a slightly negative deviation from ideality below 25 atomic percent chromium. The addition of molybdenum to the nickel-chromium-molybdenum alloy increases the chromium activity. Figure 16 shows that the effect of molybdenum is greater at lower temperatures and higher chromium contents.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In the fcc phase region of Ni-Mo system, from 1150 to 1350 K, the Mo activity presents a positive deviation from the Raoult's Law behavior. The Mo activity decreases towards ideality as temperature increases.

In the fcc phase region of Ni-Cr-Mo system, from 1150 to 1373 K, the Cr activity increases upon adding Mo into the Ni-Cr-Mo alloy. The Cr activity deviates negatively from ideality below 5 to 10 atomic percent Cr and 10 atomic percent Mo and positively above these compositions. Above these values, the Cr activity decreases to ideality as temperature increases.

The following are the recommendations by the author for continued study in this area:

1. During the preparation of yttria-doped thoria electrolyte, Mo contamination should be avoided if possible even though Mo was shown to have no significant effect on the equilibrium measurements in this study. However, the impurities-free yttria-doped thoria electrolyte used does make it possible to trace any side reaction with or diffusion of metal from electrode during the equilibrium emf measurement.
2. Each alloy to be measured should have its composition and structure at every step of preparation and emf

measurement followed because the undesired reactions such as oxidization or contamination at high temperature may occur.

3. To find a model for the solution of the Ni-Cr-Mo alloy needs more data with a great variation of compositions of Ni-Cr-Mo alloys.

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