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I am submitting herewith a thesis written by Sujit Das entitled "Part I: Study on the Performance of a Solid State Electrochemical Cell Using Yttria-Doped Thoria Electrolyte. Part II: Calculation of the Fe-Ni Phase Diagram from 1184°K to 300°K." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.

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PART I: STUDY ON THE PERFORMANCE OF A SOLID STATE ELECTROCHEMICAL
CELL USING YTTRIA-DOPED THORIA ELECTROLYTE. PART II: CALCULATION
OF THE Fe-Ni PHASE DIAGRAM FROM 1184°K TO 300°K

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Sujit Das
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DEDICATION

This thesis is dedicated to my parents, Mr. and Mrs. Hari Mohan Das.

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many ways during the last two years the author has spent in this department.

ABSTRACT

The main purpose of this investigation was to study the performance of a solid state electrochemical cell using yttria-doped thoria electrolytes, which have been extensively used these days in high temperature thermodynamic research. Attaining equilibrium for these cells was slow and required attention only about twice a day. Advantage was taken of the time available to carry out a computer and graphical calculation of the Fe-Ni phase diagram in the solid region, as the understanding of this system is of interest in understanding the behavior of superalloys. Thus, this is a two-part thesis—Part I dealing with the performance of a solid state electrochemical cell using yttria-doped thoria electrolytes and Part II with the calculation of the Fe-Ni diagram from 1184°K to 300°K.

In the solid state electrochemical cell study, yttria-doped thoria solid electrolytes have been fabricated in our laboratory using our newly developed nitrate process. Their performance was then studied by the electrochemical cell consisting of Cr-Cr₂O₃ and Ta-Ta₂O₅ as electrodes. Both a single chamber and a double chamber experimental arrangements were tried.

Yttria-doped thoria electrolytes of composition ThO₂ + 6.625 mole% Y₂O₃ made from 99.99% purity thorium nitrate and 99.9% purity yttrium nitrate powders by our newly developed nitrate process gave the best properties. Electrolytes were transparent in color and had 99.96% of the theoretical density. Pycnometrically measured densities of these fired pellets have agreed with those calculated for the anion vacancy model.

Electrolytes of composition $\text{ThO}_2 + 9.2 \text{ mole\% Y}_2\text{O}_3$ made from 99.9% purity thorium and yttrium nitrate powders by our nitrate process and also $\text{ThO}_2 + 5.3 \text{ mole\% Y}_2\text{O}_3$ electrolytes made by directly mixing respective 99.9% purity oxide powders did not give satisfactory results.

The solid state electrochemical cell using $\text{Ta-Ta}_2\text{O}_5$ and $\text{Cr-Cr}_2\text{O}_3$ as electrodes, and $\text{ThO}_2 + 6.625 \text{ mole\% Y}_2\text{O}_3$ as the electrolyte was studied. The performance of the cell was not satisfactory. Various reasons have been attributed to this failure. One of the important reasons may be the inability to obtain a p_{O_2} of the order of 10^{-25} atm. in the cell environment (particularly the $\text{Cr-Cr}_2\text{O}_3$ inner chamber). This low value of p_{O_2} corresponds to the equilibrium pressure of $\text{Ta-Ta}_2\text{O}_5$ electrode at 1000°C . The cell emf was found in general to increase with time and was very much dependent on the flow rate of the inert gas. The resistance of the cell was found high, of the order of kilo-ohms. These characteristics may be due to a new cell $\text{Ta, Ta}_2\text{O}_5/\text{YDT}/p_{\text{O}_2}$ (inner chamber) becoming operative because of the formation of a layer of Cr_2O_3 (caused by inadequate p_{O_2} atmosphere). This new cell theoretically has a larger cell emf and a lower resistance than the actual cell in consideration at that time. The emf developed across this new cell will be very much dependent on p_{O_2} in the environment of inner chamber.

In the calculation of the Fe-Ni diagram, using computer programs available in this Department, various sources of solution thermochemistry information at high temperatures (solid region) of the Fe-Ni system have been analyzed in order to determine the best fit with the most recent experimental α - γ boundary. Based on the recent pulse calorimetric measurements of C_p and the heat of the order-disorder transformation for

the Ni_3Fe alloy, the $\gamma\text{-Ni}_3\text{Fe}$ and $\alpha\text{-Ni}_3\text{Fe}$ boundaries have been determined graphically.

On the basis of the least negative data of ΔG_{γ}^M reported to this date, ΔG_{γ}^{XS} has been fitted to a Legendre polynomial; and assuming α to behave as an ideal solution, excellent agreement of the calculated $\alpha\text{-}\gamma$ boundary was obtained with the most recent experimental one. The eutectoid transformation ($\gamma \rightarrow \alpha + \text{Ni}_3\text{Fe}$ (ordered)) was found to be at 565°K and 52 at. % Ni, and the maximum solubility of nickel in the b.c.c. phase was near 9 at. %. Due to the absence of any well-established model to take into account the effect of loss of ordering with the increasing temperature on $\Delta G_{(\text{Ni}_3\text{Fe})}^F$, proper calculations could not be made with the $\gamma\text{-Ni}_3\text{Fe}$ boundary. The ordered NiFe could not be taken into consideration in our present phase boundary calculation, as no thermodynamic data are available on NiFe.

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PART I: STUDY ON THE PERFORMANCE OF A SOLID STATE
ELECTROCHEMICAL CELL USING YTTRIA-DOPED
THORIA ELECTROLYTE

CHAPTER I

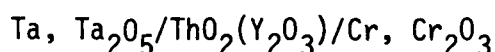
INTRODUCTION

It was proposed by Wagner (20) in 1943 that certain oxide solid solutions such as $\text{ZrO}_2\text{-CaO}$ contain vacant oxygen sites and thus can be used as solid electrolytes for the transport of oxygen ions. Although the electrolyte exhibits virtually exclusively ionic conduction at high temperatures, the electronic conduction is a significant factor below $p_{\text{O}_2} = 10^{-22}$ atm. at 1000°C , e.g., for $\text{ZrO}_2\text{-CaO}$ electrolytes (21). Solid electrolytes have superseded molten salt electrolytes as they have higher temperature range, and cells based on these electrolytes are easier to assemble and use.

During the past 23 years, oxide electrolytes based on the group IVB oxides ZrO_2 , HfO_2 , CeO_2 or ThO_2 with additions of either an alkaline earth oxide such as CaO or a rare earth oxide such as Y_2O_3 have been extensively used in the construction of galvanic cells for measuring the thermodynamics and kinetics of oxygen-containing systems with high accuracy. With solid electrolyte galvanic cells, high temperature thermodynamic measurements on solid alloys can be performed more rapidly and with a higher degree of accuracy than by the method of equilibrium of the alloy with a suitable vapor. The activity of a metal in an alloy can be measured directly with great speed and accuracy by simply measuring the voltage developed across the cell consisting of alloy-oxide and metal-oxide as electrodes. A good review exists of many investigations of many systems using oxide solid electrolytes (22).

Calcium-stabilized zirconia and yttria-doped thorium are the most commonly used solid electrolytes for the high temperature thermodynamic measurements in high oxidizing and reducing atmosphere, respectively. The activity of Ta in Ta-W alloys has been successfully measured using yttria-doped thorium as an electrolyte (23). Yttria-doped thorium electrolytes may be ionic even down to $p_{O_2} = 10^{-34}$ atm. at 1000°C. But the performance of these electrolytes is very sensitive to the purity of initial materials, composition, method of fabrication and the other experimental variables. A number of studies (12,78,79) exist in the literature on factors influencing the performance of solid oxide electrolytes in high temperature thermodynamic measurements.

A newly developed nitrate process has been used in our laboratory to fabricate yttria-doped thorium electrolytes. Their performance was then studied by studying the following cell:



where the standard free energy of formation of these oxides is well established in the literature. However, these cells will perform satisfactorily only in high reducing atmospheres where $p_{O_2} \leq 10^{-25}$ atm.

CHAPTER II

LITERATURE SURVEY

A. ELECTROCHEMISTRY OF CERAMIC ELECTROLYTES

At temperatures greater than 0°K, even an exactly stoichiometric pure binary crystalline compound has a finite concentration of point defects such as vacancies and interstitials, the presence of which lowers the Gibbs free energy. With the perfect crystal as reference, the normal atoms on the regular lattice sites have zero effective charge which for the normal cations and anions in an oxide MO are written as M_M^x and O_O^x (1,2). When vacancies are present (for example, when an oxygen atom on a normal site is removed from the crystal), the two negative actual charges, i.e., the two excess electrons of the oxygen ion, are left in the crystal. If both of these electrons are localized at the oxygen vacancy, the oxygen vacancy has two negative actual charges; the charge is the same as in a perfect crystal, and the oxygen vacancy then has zero effective charge. One or both of the localized or trapped electrons may be excited and transferred away from the neighborhood of the oxygen vacancy, and the oxygen vacancy becomes singly or doubly ionized, respectively. Since electrons are removed, the ionized oxygen vacancies will have an effective positive charge with respect to the perfect crystal. The whole process thus can be written as:



To distinguish effective from actual charges, different symbols are used. While actual charges are written + and -, the effective positive charge is indicated by a superior dot and the effective negative charge by superior prime; singly and doubly ionized vacancies are, for instance, written V_O and V_O'' , respectively. Similarly, cation vacancies may be neutral (V_M^X) or they may have effective negative charge, i.e.,



whereas interstitial cations have an effective positive charge, i.e.,



and interstitial anions have effective negative charges, i.e.,



A comprehensive list of different symbols used here with their definitions is given in Table I-1. In addition to the formation of electronic defects in connection with the formation of the point defects, for example, Equations (1) and (2), electronic defects can be formed by the thermal excitation of electrons from the valence band to the conduction band which can be expressed as:



where O designates a perfect crystal and $h^{\cdot}$ is the unoccupied electron site in the valence band (electron holes).

Frenkel and Schottky defects are the most common types of intrinsic defects in ionic solids. The Schottky defect structure

TABLE I-1
SYMBOLS USED AND THEIR DEFINITIONS

Symbol	Definition
M_M^X or M_M	Cation on a cationic lattice; neutrally charged
O_O^X or O_O	Anion (oxygen) on an anionic lattice site; neutrally charged
$V_O^\cdot$ and $V_O^{\cdot\cdot}$	Singly and doubly ionized oxygen vacancies; positively charged
V_M' and V_M''	Singly and doubly ionized cation vacancies; negatively charged
V_O^X and O_i^X	Unionized oxygen vacancy and interstitial; neutrally charged
V_M^X and M_i^X	Unionized cation vacancy and interstitial; neutrally charged
$M_i^\cdot$	Singly ionized cation interstitial; positively charged
$O_i^\cdot$	Singly ionized oxygen interstitial; negatively charged
e'	Electrons; negatively charged
$h^\cdot$	Electron holes; positively charged
n	Concentration of electrons
p	Concentration of electron holes
σ_θ	Conductivity due to electrons
$\sigma_{\oplus}$	Conductivity due to electron holes

involves the presence of equivalent amounts of cation and anion vacancies, i.e.,



whereas the Frenkel defect structures are limited either to the cations or the anions, and the disorder involves the presence of equivalent numbers of vacancies and interstitial ions in a crystal, i.e.,



Here M_M represents a cation on a cationic lattice, O_O an oxygen atom on an anionic lattice, V_O an oxygen vacancy, V_M a metal (cation) vacancy, O_i an oxygen interstitial atom, and M_i a metal interstitial atom. Schematic diagrams of these two types of defects are shown in Figures I-1 and I-2.

Useful oxide electrolytes have the fluorite structure which is shown in Figure I-3. The fluorite structure consists of a simple cubic lattice occupied by the anions with the centers of alternate cubes occupied by the cation or a f.c.c. arrangement of cations with the anions occupying all the tetrahedral sites. The unoccupied cube centers are believed to be the key to the defect and diffusion properties of these materials. It is thought the anion sublattice disorders, with anions leaving their lattice sites and moving to interstitial locations at or near these cube centers, thus forming Frenkel defects. A maximum in the specific heat supports this picture of the disorder (3). For

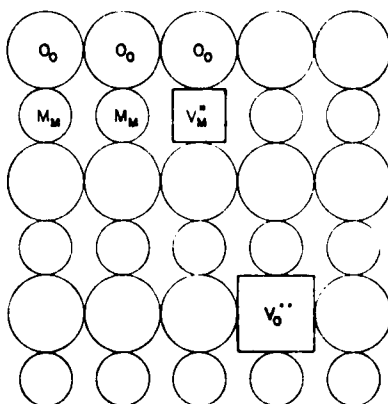


Figure I-1. Schematic illustration of Schottky disorder with equivalent concentrations of doubly charged vacancies, V_M^{2+} and V_O^{2+} in an oxide MO from Kofstad (24).

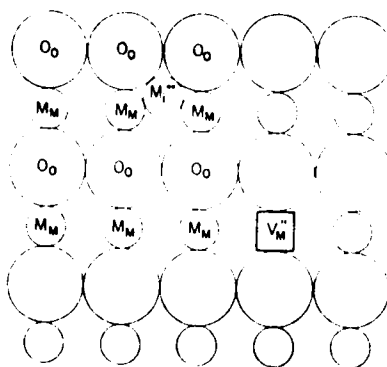
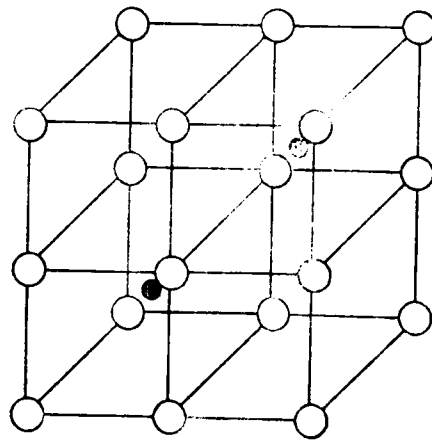


Figure I-2. Schematic illustration of Frenkel disorder involving doubly charged cation vacancies and interstitial ions in an oxide MO from Kofstad (24).



● Cation

○ Anion

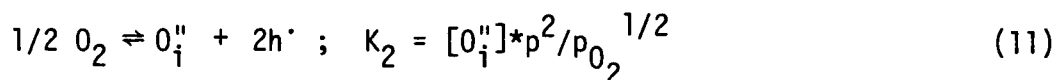
Figure I-3. The fluorite structure.

example, in the ThO_2 the predominant ionic defects are anionic Frenkel defects, which can be represented as (4,5):



where K_1 is the equilibrium constant.

When a semiconducting compound is brought into equilibrium with a gas phase containing one of the components of the compound, equilibration of the vapor with the crystal occurs by the introduction of ionic defects and compensating electronic defects. Thus, under a high oxygen pressure, the predominant defects are interstitial oxygen ions and electron holes, i.e.,



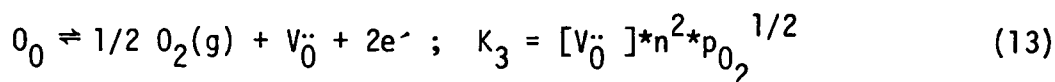
where p denotes the concentration of electron holes (i.e., $p = [\text{h}^{\cdot}]$).

If $[\text{O}_i^{\prime\prime}]$ is determined by this equilibrium, to maintain the electro-neutrality condition:

$$[\text{h}^{\cdot}] + 2[\text{V}_{\text{O}}^{\cdot\cdot}] = [\text{e}^{\cdot-}] + 2[\text{O}_i^{\prime\prime}] \quad (12)$$

$[\text{O}_i^{\prime\prime}]$ will be essentially equal to $[\text{h}^{\cdot}]/2$. Substituting this relationship into Equation (11) yields a $p_{\text{O}_2}^{1/6}$ dependence of $[\text{h}^{\cdot}]$ and hence of the conductivity due to holes $\sigma_{\oplus}$.

Similarly, at very low oxygen pressures, the predominant defects in equilibrated ThO_2 will be oxygen vacancies and electrons, i.e.,



where n denotes the concentration of electrons (i.e., $n = [\text{e}^{\cdot-}]$). If

$[V_{\text{O}}^{\bullet\bullet}]$ is determined by Equation (13), from the electroneutrality condition (12), $[V_{\text{O}}^{\bullet\bullet}] \approx [e^-]/2$ and hence the conductivity due to electrons

$$\sigma_{\theta} \propto n \propto p_{\text{O}_2}^{-1/6}.$$

In the intermediate oxygen pressure range, there will be predominantly ionic defects, the concentrations of which are independent of oxygen pressure, and the governing defect equation will be (10). A schematic representation of the dependence of ionic electrical conductivity on the oxygen pressure in the case of pure ThO_2 is shown in Figure I-4. To be pointed out in Section C of this chapter, for a compound to be a solid electrolyte, t_{ion} (i.e., the sum of anionic and cationic transference numbers) should be nearly equal to 1. Thus, in the oxygen pressure region where defects are totally ionic and independent of oxygen pressure, pure thorium can behave as a solid electrolyte.

Ceramic electrolytes usually are solid solutions of two compounds, where extrinsic defects are intentionally created to enhance ionic conduction. Transport number measurements (6) and diffusion studies (7,8) on the fluorite crystal structure show that as the temperature is increased, the cation sublattice remains nearly perfect while the anion sublattice becomes highly disordered. By doping with aliovalent impurities (i.e., impurities having valencies different from that of the normal ions), it is known that Frenkel defects are predominant and furthermore the anion vacancies are more mobile than the anion interstitials—at least in the temperature ranges accessible by this technique (9,10). The dissolution of yttria into the fluorite phase of ThO_2 can be written:

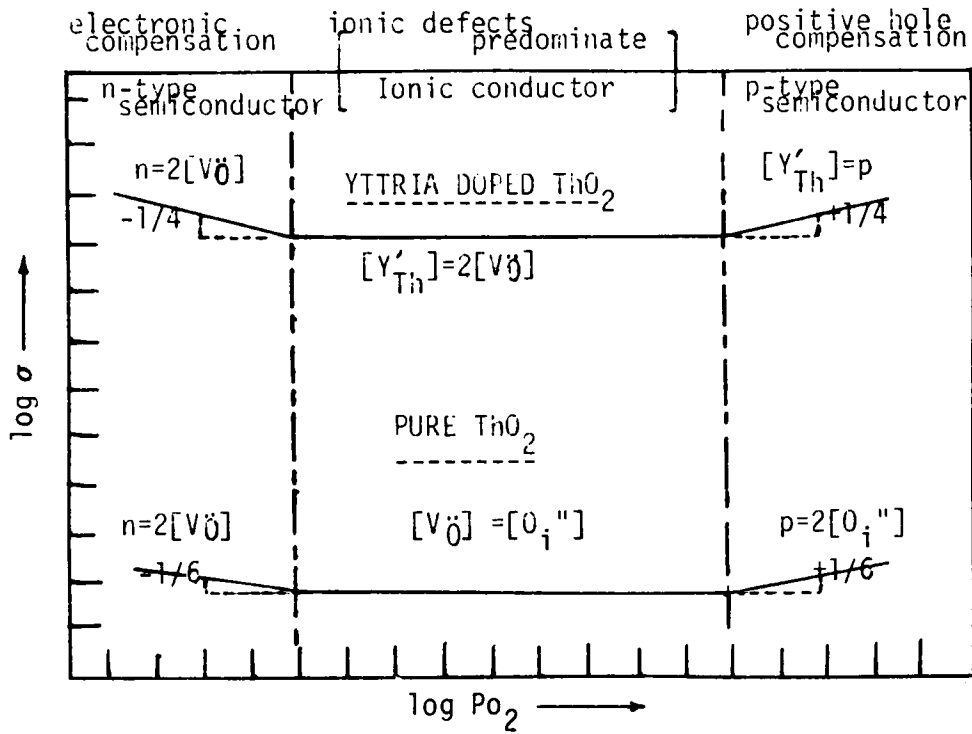
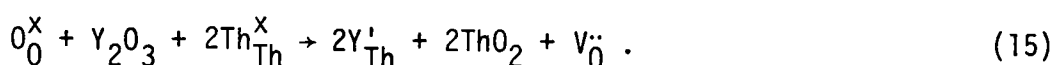


Figure I-4. Schematic representation of the variation of ionic electrical conductivities for pure ThO_2 crystal and yttria-doped thoria crystal with the partial pressure of oxygen.



Here these additional negative effective charges, i.e., $[Y'_{Th}]$, must for electroneutrality be balanced by creation of an equivalent concentration of positive effective charges. So, the net equation becomes:



Equation (15) preserves the original lattice site ratio in ThO_2 . Thus, the number of oxygen vacancies increases greatly and the general electroneutrality condition becomes:

$$p + 2[V_{\ddot{O}}] = n + 2[O_i''] + [M'_{Th}] \quad (16)$$

If $[M'_{Th}]$ is large relative to the intrinsic ionic defect concentrations, the concentration of dopant will determine the number of oxygen vacancies. The electroneutrality condition then reduces to:

$$2[V_{\ddot{O}}] \cong [M'_{Th}] \quad (17)$$

Thus, with the addition of Y_2O_3 , the conductivity due to electrons and electron holes varies directly with $p_{O_2}^{-1/4}$ and $p_{O_2}^{1/4}$, from Equations (13) and (11), respectively. This comes from the assumption that the concentration of ionic defects is much greater than that of electronic defects, so $[O_i'']$ and $[V_{\ddot{O}}]$ can be assumed to be constant. The 1/4 power dependencies of electronic conductivities for the case of yttria-doped thorium are shown in Figure I-4. At a fixed oxygen pressure, any increase in the oxygen vacancy concentration must decrease the concentration of oxygen interstitials (Equation (10)), increase the electron

hole concentration (Equation (11)), and decrease the electron concentration (Equation (13)), as is depicted in Figure I-5. Here the ionic conductivity (σ_{ion}) and the electron hole conductivity (σ_h) increase, while the electron conductivity (σ_e) decreases, with increasing Y_2O_3 content. Thus, the increased concentration of oxygen vacancies due to doping increases the p_{O_2} range of ionic conductivity as also shown in Figure I-5. A maximum value of ionic conductivity (σ_{ion}) occurs at 3.5-4% oxygen vacancies. High oxygen vacancy concentration causes a decrease due to vacancy ordering (14), vacancy clustering (15) and/or oxygen dopant vacancy interactions (16).

Plots of conductivity versus oxygen partial pressure may be extended into three dimensions by the addition of a further variable, temperature. The projection of these data onto the $\log(p_{O_2})$ versus $1/T$ plane produces a plot, various regions of which correspond to a particular type of conduction process, as shown in Figures I-6 and I-7 for a typical oxide electrolyte. The region of predominantly ionic conduction, i.e., region where $t_{ion} \geq 0.99$, is often termed the electrolytic domain, as suggested by Patterson (11). Prior knowledge of such a figure enables one to keep well within a particular region while conversely the variation of conductivity with partial pressure may give a clue to the form of the diagram. Areas close to the electrolytic domain boundary will represent mixed conduction conditions, and mobility may be the important factor in determining the ionic/electronic conductivity ratios within these areas rather than concentration values. The higher the ionic mobilities, of course, the larger will be the region of the electrolytic domain. Figure I-8 shows the electrolytic domain for

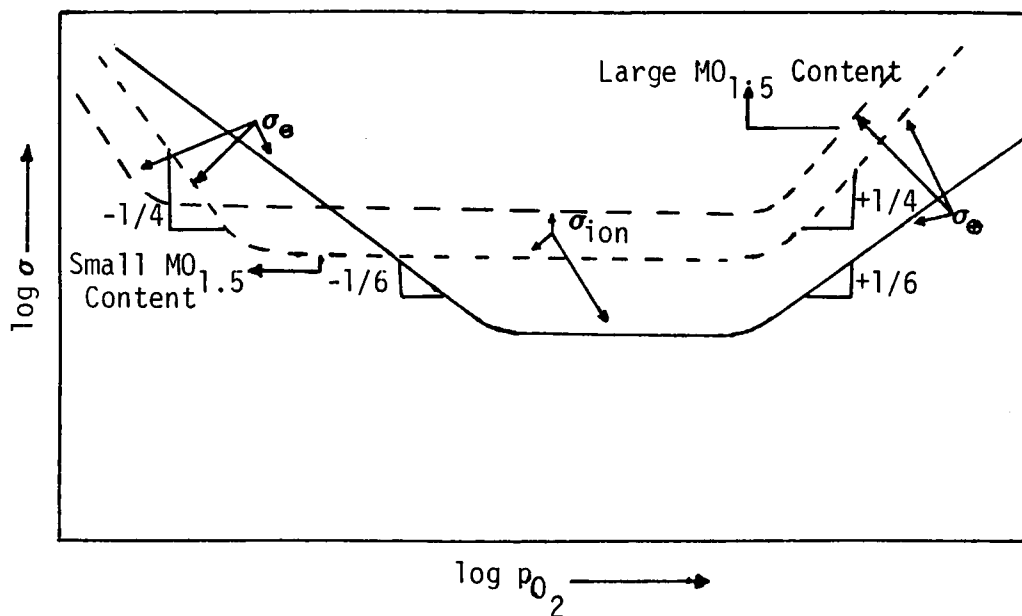


Figure I-5. Schematic illustration of the effect of dopant concentration on partial conductivities in $\text{ThO}_2\text{-M}_2\text{O}_3$ solid solutions.

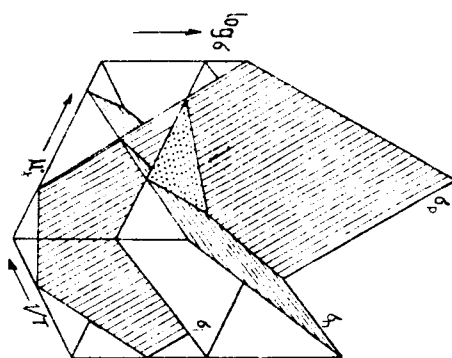


Figure I-6. Conductivity diagram after Patterson (11). Domain boundaries are given as intersections of the ionic and electronic conductivity planes (from Heyne (19)).

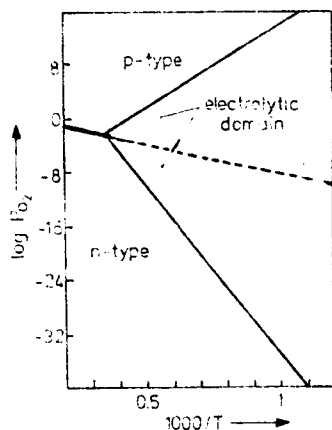


Figure I-7. Domain boundaries of stabilized zirconia as a projection on the μ_x - $1/T$ plane. i = line of intrinsic conductivity; μ_x = chemical potential of oxygen (from Heyne (19)).

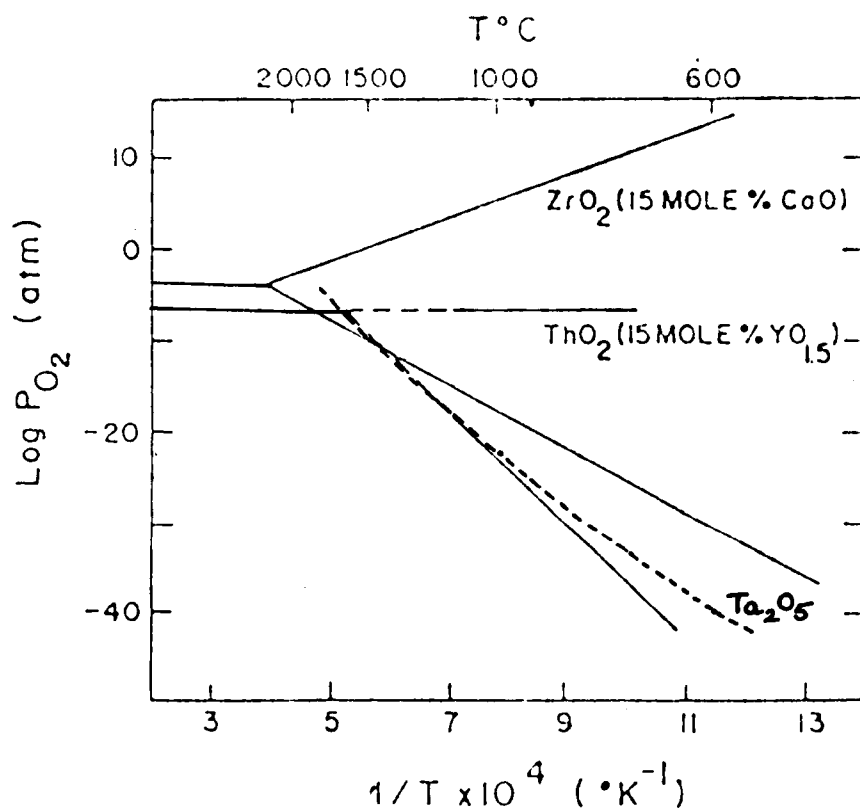


Figure I-8. Electrolytic domain for CSZ and YDT (Patterson (11)).

calcia-stabilized zirconia and yttria-doped thoria. Yttria-doped thoria exhibits significant positive hole conduction at oxygen pressures above 10^{-6} atm. at 1000°C (4,12) and remains an ionic conductor at much lower oxygen pressures ($\leq 10^{-25}$ atm. at 1000°C (13)) than calcia-stabilized zirconia. It has been suggested that YDT may be ionic, i.e., $t_{\text{ion}} \geq 0.99$ down to $p_{\text{O}_2} = 10^{-34}$ atm. at 1000°C (17); other authors report an influence of electronic conduction on emf results at 10^{-29} atm. (18). Zirconia electrolytes (17) exhibit n-type electronic conductivity at an oxygen pressure below 10^{-22} atm. at 1000°C and there is no significant positive hole conduction up to at least $p_{\text{O}_2} = 1$ atm. at 1000°C . Thus thoria electrolytes cannot be used in high p_{O_2} environments such as air and zirconia electrolytes will be partially electronic conductors in highly reducing atmospheres.

In our present research the equilibrium partial pressure of oxygen is as low as 10^{-25} atm. at 1000°C , corresponding to the Ta, Ta_2O_5 electrode, as seen from Figure I-8, where the plot of variation of partial pressure of oxygen with temperature for the formation of Ta_2O_5 has been superimposed on the electrolytic domain diagram of Patterson (11). The equilibrium partial pressure of oxygen in the case of Cr- Cr_2O_3 electrode is 10^{-23} atm. at 1000°C . Thus, the electrochemical cell involving Ta- Ta_2O_5 and Cr- Cr_2O_3 as electrodes is well suited to study the performance of YDT electrolytes.

B. PROPERTIES AND APPLICABILITY OF VARIOUS CERAMIC ELECTROLYTES

Comprehensive lists of over 30 solid electrolytes have been compiled (30,32) and their electrical properties have been extensively

reviewed by Etsell and Flengas (22). Solid halides such as NaCl, KCl, AgCl or AgBr, etc. are examples of pure solid electrolytes. The most useful halide electrolyte for high temperature research is CaF_2 .

The ceramic electrolytes can be separated into three groups. The first group includes AgI, RbAg_4I_5 and $\text{Ag}_6\text{I}_4\text{WO}_4$ which exhibit remarkable high conductivities at low temperatures. Beta alumina electrolytes ($\text{NaAl}_{11}\text{O}_{17}$, $\text{AgAl}_{11}\text{O}_{17}$, $\text{KAl}_{11}\text{O}_{17}$, etc.) comprise the second group of useful electrolytes. As shown in Figure I-9, these $\beta\text{-Al}_2\text{O}_3$ electrolytes have high values of ionic conductivity over the temperature range 600-800°C. These conductivities are independent of oxygen partial pressure from 0.2 to 10^{-24} atm. (33). These electrolytes not only have excellent potential applications in batteries and as chemical probes but also are extremely useful in high temperature research.

The third group of useful electrolytes comprise CaF_2 , ZrO_2 -based and ThO_2 -based electrolytes. The fluorite crystal structure is a f.c.c. arrangement of cations with the anions occupying all the tetrahedral sites. Electrical conduction in CaF_2 is ionic with the F^- ion carrying all the current. The useful temperature range of CaF_2 is 400-1000°C. The low temperature limit is fixed by the resistivity of CaF_2 and the high temperature limit by vaporization of fluorine. High temperature electrochemical cell measurements with metal-metal fluoride electrodes have been summarized by Skelton and Patterson (34).

Zirconia and thoria-based solid solutions are most widely used in high temperature research. ZrO_2 , which is monoclinic at a temperature less than 1000°C, can readily be stabilized in the cubic form

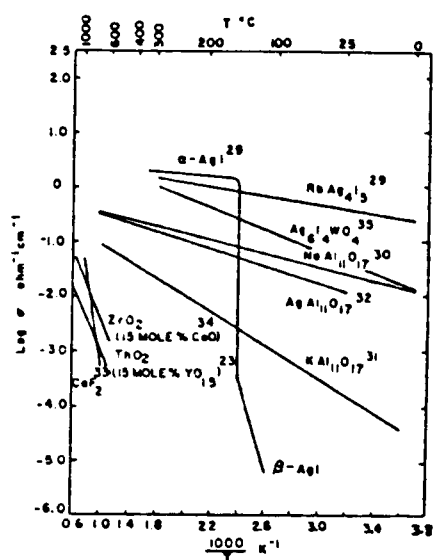


Figure I-9. Ionic conductivity as a function of temperature for various solid electrolytes (76).

by the addition of the oxides of lower valence metals (35). A maximum conductivity of about $5.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1000°C is obtained with 12-13% CaO. This is also a minimum amount of CaO necessary to stabilize cubic ZrO_2 . Several ternary systems involving ZrO_2 and CaO have been studied. Addition of both MgO (35) and Y_2O_3 (15) increased the conductivity, probably owing to the reduced lattice distortion in the case of MgO because of the relatively small Mg^{2+} ions and weaker defect interactions in the case of Y_2O_3 . Other less important ZrO_2 based electrolytes are $\text{ZrO}_2 + 10\% \text{ Sm}_2\text{O}_3$, $\text{ZrO}_2 + 8\% \text{ Yb}_2\text{O}_3$, $\text{ZrO}_2 + 10\% \text{ Sc}_2\text{O}_3$, etc. $\text{ZrO}_2 + 10\% \text{ Sc}_2\text{O}_3$ has a maximum ionic conductivity of $25 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1000°C (15,37). These electrolytes are widely used in high temperature thermodynamic property measurements; for use as an oxygen getter in a gas stream (39); for use as an oxygen partial pressure gauge (38); in fuel cells (40); and as oxygen activity probes in liquid metal baths (41).

Among the ThO_2 -based electrolytes, $\text{ThO}_2\text{-Y}_2\text{O}_3$ is the most important one. The ionic conductivity reaches a maximum at about 8 mole % Y_2O_3 or 3.7% anion vacancies (5,12) as shown in Figure I-10. Both ionic and p-type conductivity increase with the Y_2O_3 content, but measurable p-type conductivity appears above an oxygen pressure of 10^{-6} atm. for 8% Y_2O_3 . ZrO_2 -based electrolytes have conductivities which are one to two orders of magnitude higher than those of the corresponding ThO_2 -based electrolytes. The major advantage of ThO_2 -based electrolytes over ZrO_2 -based ones is their ionic conductivity under highly reducing conditions. This is important at high temperatures ($1200\text{--}1600^\circ\text{C}$) and low p_{O_2} 's where n type conductivity can seriously impair the performance of

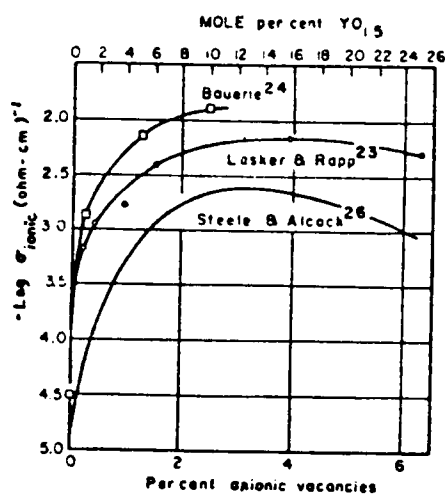


Figure I-10. Ionic conductivity of $\text{ThO}_2(\text{Y}_2\text{O}_3)$ as a function of oxygen vacancy concentration at 1000°C (76).

ZrO₂-based electrolytes. This is evident from Figure I-8 (p. 16) and Figure I-11. The p-n transition occurs at oxygen pressure of 10^{-12} and 10^{-8} atm. at temperatures of 1400°C and 1600°C, respectively (42).

Thermodynamic properties of the system US-UOS-UO₂ have been investigated by Yuill and Cater (43) using ThO₂-7% Y₂O₃ and using Ta-Ta₂O₅ as a reference electrode in the temperature range of 780-1085°C. Thoria-based electrolytes have also been used to measure oxygen pressures in gas mixtures (44); the oxygen activity in liquid iron (45); as a reference electrode in KCl-NaCl-Na₂O melts (46); and as elements in oxide resistor furnaces (47). Low conductivities (e.g., $0.23 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1000°C for ThO₂ + 8.1 mole% YO_{1.5} (12)) and the presence of p-type conductivity at high oxygen pressure preclude their use in fuel cells. Thermodynamic properties in the Ta-Mo (66) and Ta-W (23) systems have been successfully investigated using thoria-based yttria electrolytes.

C. HIGH TEMPERATURE THERMODYNAMIC MEASUREMENTS BY SOLID STATE ELECTROCHEMICAL CELLS

Thermodynamic measurements based on electrochemical cells with solid oxide electrolytes have been extensively reviewed (22,28,30,48,49). Chemical potentials of oxygen in oxides and in metals, the thermodynamic stabilities of oxides and intermetallic compounds and thermodynamic properties of alloys have been measured.

The thermodynamic measurements are based on the relation between the electromotive force (E) of an electrochemical cell and the chemical potential (μ_X) of nonmetal X at each electrode, derived by Wagner (25),

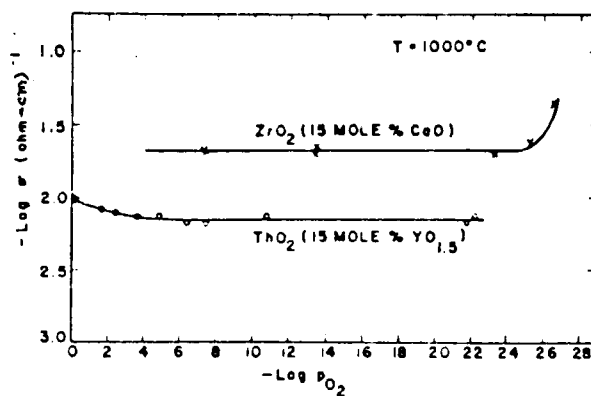
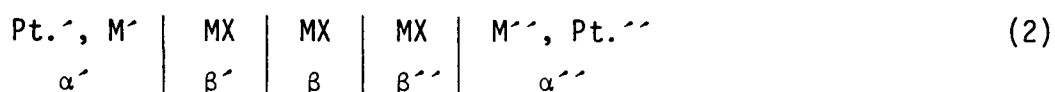


Figure I-11. Electrical conductivity of $\text{ZrO}_2(\text{CaO})$ and $\text{ThO}_2(\text{Y}_2\text{O}_3)$ as a function of oxygen partial pressure at 1000°C (76).

$$E = - \frac{1}{|Z_X|F} \int_{\mu_X}^{\mu_X'} t_{ion} d\mu_X \quad (1)$$

where F is Faraday's constant, $|Z_X|$ is the absolute value of the valence of the X ion in the electrolyte and t_{ion} is the ionic transference number, which is the fraction of current carried by ionic carriers. The relationships between the emf and associated free energy is derived from the following concentration type cell incorporating the solid electrolyte, MX (β phase) and two electrodes (α phase) reversible to the same ionic species, M^+ ,



Here β' and β'' are the portions of the electrolyte (β) which are in contact with the two electrodes α' and α'' , respectively, and Pt. serves only to promote contact of the emf measuring leads with the electrodes. As seen from Figure I-12 of the representation of the galvanic potentials, ϕ , across the galvanic cell the maximum galvanic potential differences occur within the interfacial boundary regions (β' and β''). Then, we have:

$$\text{Electromotive force (E)} = (\phi_{\alpha''}' - \phi_{\alpha}') = -1/F[(\bar{\mu}_e)_{\alpha''}' - (\bar{\mu}_e)_{\alpha}'] \quad (3)$$

$$= (\phi_{\alpha''}' - \phi_{\beta''}') + (\phi_{\beta''}' - \phi_{\beta}') + (\phi_{\beta}' - \phi_{\alpha}') \quad (4)$$

Assuming electrochemical equilibrium established at the α''/β'' interface for,



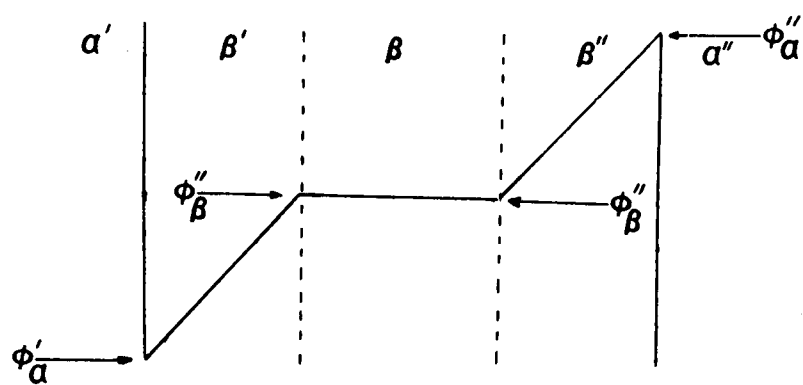


Figure I-12. Schematic representation of the galvanic potentials ϕ across the galvanic cell.

it can be derived (26) that,

$$E = -(1/F)[(\mu_M)_{\alpha}^{\prime\prime} - (\mu_M)_{\alpha}^{\prime}] + (1/F)[(\bar{\mu}_{M+})_{\beta}^{\prime\prime} - (\bar{\mu}_{M+})_{\beta}^{\prime}] . \quad (6)$$

The second term in Equation (6) represents the difference in the electrochemical potential of the ionic species (M^+) established within the solid electrolyte phase (β) in contact with the interfacial regions at the right- and left-hand side. This is due to the variation of the electrochemical potentials of the ionic species across the electrolyte phase. So the irreversible diffusion processes involving the transfer of ionic species between different concentration levels which are characterized by the existence of a diffusion or (junction) potential must be taken into account. Using irreversible thermodynamics (27,31), the second term reduces to:

$$1/F \int_{\beta}^{\beta\prime\prime} \sum t_i [-(1/Z_i) * d\bar{\mu}_i + d\bar{\mu}_{M+}] \quad (7)$$

where t_i is the transference number of the i^{th} ionic species with respect to an appropriate reference frame such as the crystal lattice in the case of a solid electrolyte. Assuming only small deviations from the stoichiometric electrolyte composition such that $d\mu_{MX} \cong 0$, then the expression for the diffusion potential simplifies to:

$$1/F \int_{\beta}^{\beta\prime\prime} t_e (d\bar{\mu}_e + d\bar{\mu}_{M+}) = 1/F \int_{\beta}^{\beta\prime\prime} t_e d\mu_M . \quad (8)$$

Under these conditions the emf of the cell is given by:

$$E = -1/F[(\mu_M)_{\alpha}^{\sim\sim} - (\mu_M)_{\alpha}^{\sim}] + 1/F \int_{(\mu_M)_{\alpha}^{\sim}}^{(\mu_M)_{\alpha}^{\sim\sim}} t_e d\mu_M \quad (9)$$

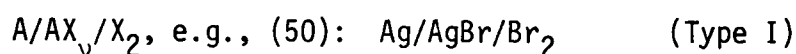
$$= -1/F \int_{(\mu_M)_{\alpha}^{\sim}}^{(\mu_M)_{\alpha}^{\sim\sim}} t_{ion} d\mu_M. \quad (10)$$

If $t_{ion} \cong 1$, then Equation (10) reduces to:

$$\Delta G = (\mu_M)_{\alpha}^{\sim\sim} - (\mu_M)_{\alpha}^{\sim} = -|Z_M|FE. \quad (11)$$

Equation (11) can also be obtained by assuming the second term in Equation (6) is negligible. This equation then can be used directly to determine the thermodynamic quantities as discussed below. Equation (11) is valid when $t_{ion} \cong 1$ and all intensive parameters such as temperature, pressure and composition, etc. of the electrochemical system are kept constant. A discussion of these points in connection with metallurgical thermodynamics can be found in the papers by Chipman et al. (29) and Rapp et al. (30). For a determination of thermodynamic quantities, galvanic cells (with electrolytes of locally variable composition) are not recommended since additional knowledge about transference numbers as a function of composition of the electrolyte is necessary to evaluate thermodynamic values from the measured emf data (27).

The simplest type of galvanic cell is the so-called formation type cell, i.e.,

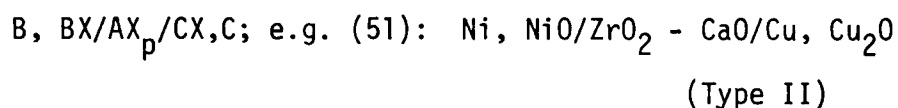


On passing $Z_A F$ coulombs, the virtual cell reaction is the formation of

AX_v from A and X_2 . Thus, if all the parts of the cell are in their respective standard states, then

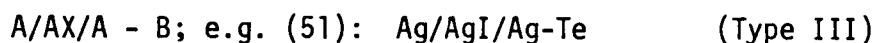
$$\Delta G = \Delta G_{AX}^{\circ} = -Z_A EF .$$

Using AX_p as the electrolyte, one may construct a displacement type cell as follows:



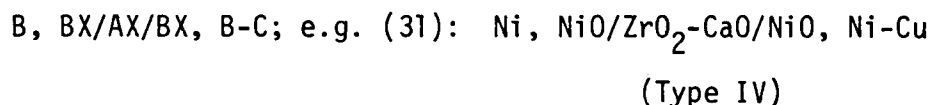
This type of cell involving in particular the oxide solutions ZrO_2 -CaO, ThO_2 - Y_2O_3 and alkaline earth fluorides as solid electrolytes has been extensively used in metallurgical thermodynamics (52-54) in the past 25 years. The Gibbs free energies of formation of many binary oxides and a number of ternary oxides have been determined in this way (55-59). A number of reference electrode systems have been established for oxygen concentration cells and data for most of these have been collected in a review article by Rapp and Shores (30).

Solid electrolytes have been used to determine the partial molar free energies and activities of components in binary alloys. The most general type of the cell is:



Since ΔG is given by a transfer of A from its standard state into the A-B alloy, $-Z_A EF$ corresponds directly to $RT \ln a_A$. The activity of alloy components can also be determined with the displacement type cell II using solid electrolytes such as CaO-stabilized zirconia, where alloy

activities at high temperatures can be determined, i.e.

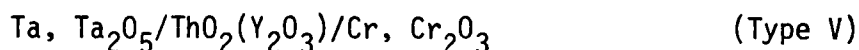


As before, $\Delta G = RT \ln a_B = -Z_B EF$. The emf so generated can only be interpreted to yield the activity of a metal in the electrode provided the oxide has a very narrow range of nonstoichiometry or there exists relatively complete information about the metal and oxygen potentials in nonstoichiometric oxide.

In this type of cell, only alloys can be studied where the difference in standard free energies of formation of the oxides of the two alloy components is large. Due to this fact, only noble metal-transition metal systems such as Pt-Ni, Pt-Co, Pd-Ni, Pd-Co, Au-Ni, etc. (54,60-65) and systems such as Ta-Mo (52), Ta-W (23), and Cu-Ni (67) have been investigated by means of cell type IV. On the basis of these same principles, oxygen activities in many liquid metals (Fe, Cu, Co, Ni, Ag, Pb, Na, etc.), liquid alloys and slag systems have been investigated with zirconia- and thoria-based electrolytes (41,68-74).

Auxiliary halide and oxide solid electrolytes have been used to obtain the thermodynamic properties of chalcogenide, carbide or nitride systems at elevated temperatures, e.g., Ag/AgI/Ag₂Se/Se-Au/C. The Gibbs free energies of formation of carbides have been found (75) using cells of type Th, ThF₄/CaF₂/ThF₄, ThC₂, C.

In the present study, the check cell of type II:



was studied where the electromotive force (E) of the cell is related to the difference in the standard free energy of formation of Cr_2O_3 and Ta_2O_5 . The standard free energy of formation of Cr_2O_3 and Ta_2O_5 are well established and the data of Mazandarany et al. (77) and Rapp et al. (30), respectively, were used here for calculation.

CHAPTER III

EXPERIMENTAL PROCEDURE

A. ELECTRODE AND ELECTROLYTE PREPARATION

Reference Electrodes

Purity of the constituents of Ta-Ta₂O₅ and Cr-Cr₂O₃ electrodes are as follows, as given by the supplier:

Tantalum	(99.90%)
Chromium	(99.95%)
Chromium Oxide	(99.80%)
Tantalum Pentaoxide	(99.95%)

All these materials were obtained from Cerac Inc. Except Cr₂O₃, all other materials were of -325 mesh size ($\leq 44 \mu$); Cr₂O₃ powders were of size $\leq 5 \mu$. Green Cr-Cr₂O₃ electrodes of 1/4" diameter and 3/8" thickness were prepared by mixing metal:oxide in the ratio 10:1 and then compacting at a pressure of 60,000 psi in a steel die. It was very difficult to obtain green Cr-Cr₂O₃ electrodes of sufficient strength. Optimum strength was obtained by adding a few drops of methanol before compacting and then compacting under a higher pressure of 80,000 psi. Green Ta-Ta₂O₅ electrodes of 3/8" diameter and 1/4" thickness were prepared by mixing Ta with Ta₂O₅ in a 10/1 weight ratio and compressing in a steel die at about 60,000 psi. The high ratio of metal to oxide was used in both the electrodes to safeguard against the possibility of metal in the electrodes being completely oxidized by small amounts of oxygen in the environment.

At first, Ta-Ta₂O₅ pellets were sintered at about 925°C for 1 day and Cr-Cr₂O₃ at 1100°C for 3 days, all in a flowing atmosphere of high purity (99.995%) argon. With these electrodes, no satisfactory results could be obtained. Subsequently Ta-Ta₂O₅ and Cr-Cr₂O₃ pellets were sintered at Oak Ridge National Laboratory at a higher temperature of 1400°C for a day in a flowing atmosphere of argon. In all the electrodes, the presence of equilibrium phases were verified from their x-ray diffractometer patterns.

Electrolytes

As shown in Figure I-10 (p. 21), the maximum conductivity in the yttria-doped thoria electrolytes is obtained with about 9-13 mole% yttria (Y₂O₃)* At first, the electrolytes were made of composition ThO₂ + 9.2 mole% Y₂O₃ by dissolving 99.9% purity Th(NO₃)₄·4H₂O with Y(NO₃)₃·6H₂O (99.9% purity) powders in a weight ratio of approximately 8:1 in distilled water and then evaporating to dryness. The thorium and yttrium nitrate powders were obtained from Mallinckrodt Co. and Alfa Ventron Co., respectively. During evaporation, the liquid was thoroughly stirred so that there was no concentration gradient in the precipitated solid solution powders of YDT. Next, these powders were ground, thoroughly mixed and finally sieved through a -325 mesh sieve. Pellets of about 1/2" diameter were then made by compacting these powders at a pressure of about 20,000 psi. Green pellets were then heated in air at a temperature of about 700°C for a sufficient length

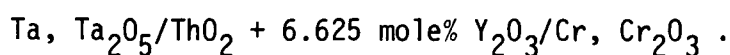
*The literature generally refers to yttria as Y₂O₃ instead of Y₂O₃.

of time (24 hrs.) to remove the last traces of NO_2 in the pellets. The pellets were sintered in covered thoria crucibles obtained from CERAC Incorporated, in order to avoid contact with undesirable species in the vapor phase. Sintering was done at a temperature of about 2000°C for 7 hrs. in a vacuum of 10^{-8} atm. Because of the poor thermal shock resistance of thoria, it was necessary to heat and cool the pellets at a very slow rate of 100°C/hr. to prevent them from developing micro-cracks. Pure thoria powders were used as spacer material to prevent the green pellets from sticking to each other during sintering. Finally, the sintered pellets were heated at about 900°C in air at first and then in a flowing atmosphere of high purity argon for several hours so as to bring the electrolytes within the working range of p_{O_2} for emf measurements.

Using the same procedure as before, electrolytes of composition $\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$ and $3/8"$ diameter were made from 99.99% purity thorium nitrate and 99.9% purity yttrium nitrate powders. This high purity thorium nitrate powder was obtained from SPEX Chemicals. Electrolytes were also made of composition $\text{ThO}_2 + 5.3 \text{ mole\% } \text{Y}_2\text{O}_3$ by directly mixing the respective commercial 99.9% purity powders.

B. EXPERIMENTAL SETUP AND OTHER DETAILS

The emf cell under study here was:



A schematic diagram of the single chamber experimental setup is shown in Figure I-13. At first, the inert gas enters the purification

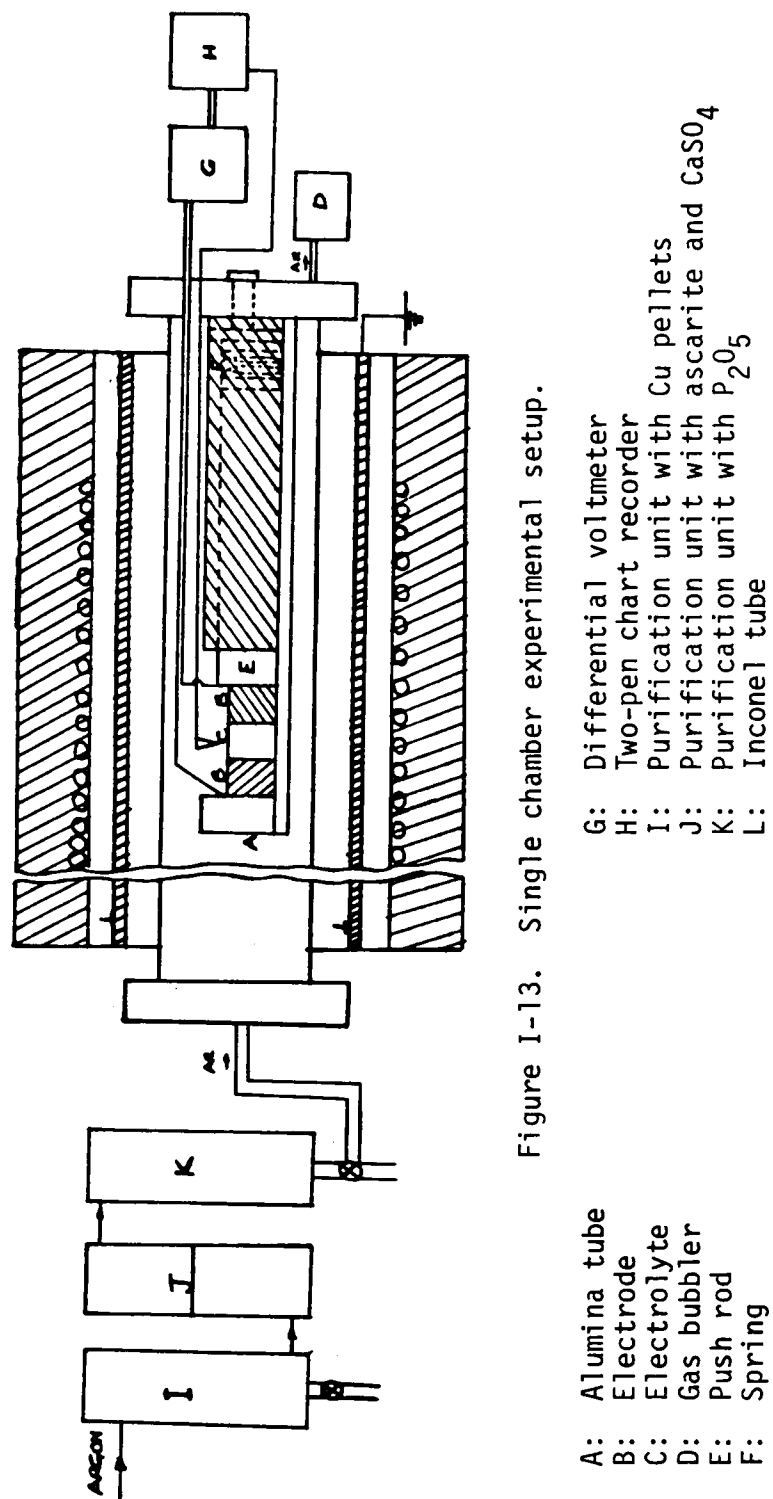


Figure I-13. Single chamber experimental setup.

column of Cu pellets heated to about 120°C, to remove the oxygen present in the gas. The next purification column consists half of ascarite and half of CaSO_4 to remove CO_2 and moisture, respectively, from the gas. Finally, the inert gas passes through the last purification column of P_2O_5 to remove the last traces of moisture present in the gas. Tantalum foils as oxygen getters were used upstream from and in the vicinity of the emf cell.

Next, the gas enters the furnace. The cell is placed inside the alumina tube A which has a push rod E of alumina and a spring F to maintain pressure on the cell and promote good contact between the electrode and electrolyte. To promote contact of the emf measuring leads with the electrodes, the leads were welded to platinum mesh. The emf was measured by a differential voltmeter G which reduces the external current flow due to its high internal impedance ($\geq 10^9 \Omega$) and potentiometric method of operation. Temperature and the cell emf were simultaneously recorded on a double pen strip chart recorder H.

Electrodes and the electrolyte were at first polished on emery paper, then on a diamond-impregnated surface to 6 μ diamond paste to achieve a mirror finish. Before assembling the cell, electrode-electrolyte contacts were verified by placing a light source behind the cell and checking that the light did not pass through the interface. If this condition is met, contact should be good enough to prevent significant interactions with the gas phase.

Before starting the experiment, the whole system was evacuated by means of a vacuum pump. A vacuum of less than 10^{-6} atm. was obtained to check that the system is substantially gas tight. After

this has been achieved, the cell was slowly heated to 200°C with the vacuum pump on. This further helped in degassing the system. Now with the vacuum pump on, argon gas was flushed on and off several times. Next, the vacuum pump was switched off and argon gas (99.995%) was passed through the system. The flow rate of the gas was high initially later being reduced to 2-3 cm³/min. The gas leaves the system through the bubbler D.

Now the temperature was raised, the temperature and emf of the cell was simultaneously recorded on a double pen strip chart recorder H over the experimental temperature range. The emfs were measured at regular intervals; and a particular temperature was maintained for a sufficient length of time so as to obtain the equilibrium values.

Previous studies (12,77,80,81) indicate that the separation of the electrodes into two compartments help to minimize oxygen transport in the gas phase from one electrode to another. Based on this idea, the modified two chamber galvanic cell has been designed as shown in Figure I-14. A mullite tube k encloses the Cr-Cr₂O₃ electrode and thus completely separates this electrode from the outside environment. An alumina tube m carrying the emf lead of this inner electrode helps to maintain the good contact with the electrolyte and also serves as an exit chamber for the gas. The cell is fixed at the end of alumina tube i by the compression spring s, transmitted through metal push tube l, and the mullite tube k. The gas enters the outside chamber at v and leaves out through bubbler n. The diameter of the metal ring t is sufficiently larger than the diameter of alumina tube m to cause easy flow of the gas into the inner chamber. The flow rate of the gas in

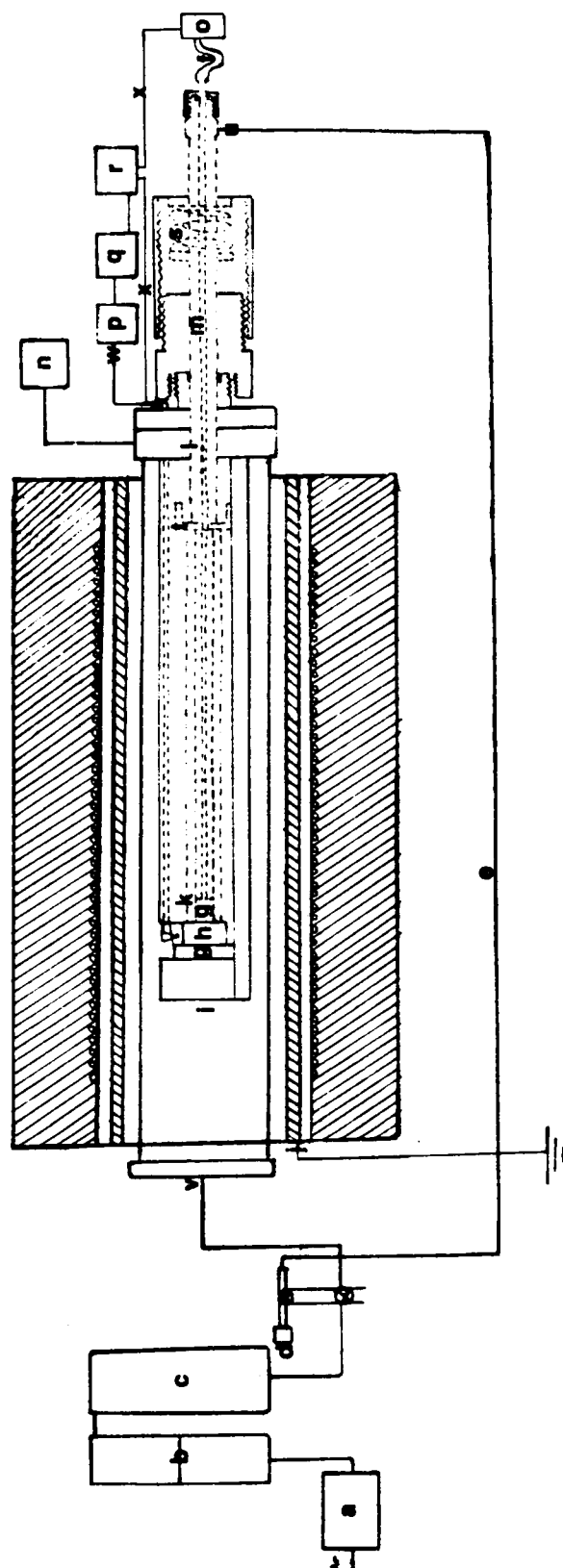


Figure I-14. Double chamber experimental setup.

- | | | | |
|-------|---|----|--|
| a: | Copper turnings at 400°C | m: | Alumina tube with emf lead for inner electrode |
| b: | Purification unit with ascarite and CaSO_4 | n: | Gas bubbler for outer chamber |
| c: | Purification unit with P_2O_5 | o: | Gas bubbler for inner chamber |
| d: | Vacuum gauge | p: | Differential amplifier |
| e, f: | Rubber tubing | q: | Two-pen chart recorder |
| g: | Electrodes | r: | Differential voltmeter |
| h: | Electrolyte | s: | Compression spring |
| i: | Alumina tube | t: | Metal ring |
| j: | Inconel tube | u: | Gas entrance for inner chamber |
| k: | Inner mullite tube | v: | Gas entrance for outer chamber |
| l: | Metal push tube | w: | Temperature leads |
| | | x: | Emf leads |

both these chambers was controlled by the two-way stopcocks placed just before the bubblers n and o. Temperature measuring leads w were connected to the two pen chart recorders q through the differential amplifier p. This differential amplifier helped in isolating the temperature and the emf. In this double chamber experimental setup, the purification column a containing Cu turnings was heated to 400°C to remove oxygen present in the gas.

To check the equilibrium cell voltage, the same value should be obtained at any particular temperature whether this temperature is reached by increasing or decreasing the temperature. The reversibility of the stable emf at any temperature should be tested by passing a small current through the cell in either direction. If reversibility has been attained, after a small current flow through the cell in either direction, the cell voltage should return to its original value. Moreover, the equilibrium cell emf should be independent of the flow rate of argon, as otherwise a mixed potential at the electrode-electrolyte interface due to the oxygen may exist.

C. EXPERIMENTAL PROBLEMS

In Preparation of Electrode

There was difficulty in getting the green pellets of $\text{Cr-Cr}_2\text{O}_3$ of sufficient strength. Application of high pressure of about 80,000 psi and adding a few drops of methanol before compacting helped to some extent in getting green pellets of sufficient strength. A sintering temperature of 925°C for 2-3 days for these electrodes did not produce enough compaction so that they could be polished even on 1/0 grit rough

emery paper. Thus, these electrodes were subsequently sintered at a higher temperature of 1400°C for a day in an inert atmosphere of argon at Oak Ridge National Laboratory.

In Preparation of Electrolyte

Although it has been suggested (21) that Y_2O_3 - ThO_2 electrolyte may be ionic down to $p_{O_2} = 10^{-34}$ atm. at 1000°C, the exact value depends on the purity of the electrolyte and on fabrication conditions. Assuming that the electronic mobility is 1000 times greater than the ionic mobility, it takes only 60 ppm of an impurity (which is compensated for by excess electrons) to introduce significant n type electronic conduction in a YDT electrolyte with 3 mole% oxygen vacancies. If there is electronic conduction, there will be weight gain at the Ta-Ta₂O₅ electrode due to the transport of oxygen ions to the Ta-Ta₂O₅ electrode, countercurrent to the electron flow. Due to the high reactivity of nitrate, from the initial stage of dissolving the nitrates in distilled water till the heating of the precipitated solid solution $ThO_2(Y_2O_3)$ powders at 700°C, extra precautions should be taken in handling of these powders, such as using glass or high purity alumina wares as much as possible.

Porosities and microcracks in the sintered electrolytes may finally provide paths for the migration of molecular oxygen from one electrode to the other and thus change the oxygen chemical potentials at the two electrode-electrolyte interfaces. So, the compacting pressure should in no case exceed 20,000 psi for the green pellets made from the precipitated solid solution powders of $ThO_2(Y_2O_3)$. A compacting

pressure of 25,000 psi resulted in cracks to the sintered electrolytes. Moreover, a slow heating and cooling rate of 100°C/hr. should be maintained during sintering in order to avoid cracking.

At low oxygen chemical potentials, there is a possibility of electronic conduction through the electrolyte, as shown in Figure I-5 (p. 15). The electronic conduction will not only reduce the cell voltage but will allow oxygen ions to be transported to the Ta-Ta₂O₅ electrode. This may lead to a different oxygen chemical potential than that established by the metal-metal oxide equilibrium. There will be oxidation at the lower p_{O_2} interface and reduction at the higher p_{O_2} interface. Recent measurements with various metal-metal oxide electrodes (76,82) have demonstrated that a steady state overvoltage is obtained when extremely small currents (1-100 μ a) are passed through symmetrical electrochemical cells of the type: M, MO/ZrO₂-CaO/M, MO. Thus, yttria should be doped with thorium in such a proportion that the composition of the electrolyte falls within the maximum ionic conductivity range as shown in Figure I-10 (p. 21). Due to the uncertainty about the actual number of molecules of hydration in thorium and yttrium nitrate powders, initially prepared ThO₂ + 7.5 mole% Y₂O₃ electrolytes showed a composition of ThO₂ + 6.625 mole% Y₂O₃ by x-ray diffraction pattern. So, initially nitrate powders should be mixed in such a proportion that takes into account the uncertainty about the actual number of molecules of hydration in thorium and yttrium nitrate powders.

In Operation of the Cell

a. Interaction of Electrodes with Gas Stream

As the equilibrium partial pressure of oxygen for Ta to form Ta_2O_5 is about 10^{-25} atm. at 1000°C , the whole experiment setup should be air tight to prevent oxygen leaks and the experiment should be carried out under a flow of high purity argon. A purity of argon as low as 10^{-25} atm. of oxygen has been obtained when the high purity argon was purified by passing through two columns of activated Linde 3A molecular sieve at room temperature (dehydrating agent), through a column of copper gauze at 500°C (primary deoxidizing agent) and finally through a titanium chip trap at 850°C (secondary deoxidizing agent) (85). In our present study, tantalum foils as internal oxygen getters were used upstream in both the inner and outer chambers and in the vicinity of the emf cell. Moreover, the double chamber cell was designed with an improved purification column consisting of copper turnings heated to 400°C .

The oxygen in the inert gas may establish a mixed potential at the electrode-electrolyte interface if good solid-solid contact does not exist at the interface so that leaking occurs. This problem can be eliminated by careful polishing of electrodes and electrolytes. Contact surfaces were polished to a mirror finish using diamond paste. Spring loading was used to promote intimate contact between the electrode and the electrolyte. A platinum o ring was also used at the interface of $\text{Cr-Cr}_2\text{O}_3$ and the electrolyte to reduce the effect of mixed potential. Poor contact resulted in a drop in the emf and the emf was not independent of the flow rate.

b. Interaction of Electrodes

Any reaction within the electrode can lead to chemical potential variation in the electrode. When using alloy oxide electrodes, one can prevent internal reaction between the alloy and oxide by using only those alloys in which metal oxide is at least 20 Kcal/mole more stable than the other. If the two oxides can form solid solutions, then the difference in ΔG_f^0 of the oxides should be even greater. In the displacement type of cell studied here, there is little probability of any exchange reaction in the electrodes.

c. Interaction of Electrode with Electrolyte

Yttria-doped thoria (YDT) electrolyte is normally inert to solid-solid reactions at high temperature. Worrell (13) has indicated a YFe_2O_3 phase on a YDT electrolyte surface, which indicated that a reaction occurs between the Fe-FeO electrode and the electrolyte. Such side reactions change the oxygen potential at the electrode-electrolyte interface and result in incorrect cell emfs. No report has so far appeared of interaction of Ta-Ta₂O₅ or Cr-Cr₂O₃ with an YDT electrolyte. In our studies too, no interaction of Ta-Ta₂O₅ or Cr-Cr₂O₃ with an YDT electrolyte was found.

d. Temperature Gradient Across the Cell

The effects of the temperature gradient within a cell add another source of emf to that determined by the electrodes. The Seebeck coefficient which measures this effect for unit temperature gradient has been studied mainly with gas electrodes and with symmetrical cells. The Seebeck coefficient was found to be a function of the absolute magnitude of the oxygen potentials of the electrodes in the case of

oxide electrolytes. Using $\text{ZrO}_2\text{-CaO}$ as the electrolyte and oxygen electrodes, a temperature difference of 1°C between the two electrodes resulted in a change of the emf of about $1/2$ mv (84). Alcock et al. (83) measured Seebeck coefficient of $(0.15 \text{ CaO} + 0.85 \text{ ZrO}_2)$ electrolyte in the temperature range of $1300\text{-}1625^\circ\text{K}$ with pure oxygen (1 atm.) as two electrodes maintained at different temperatures to be -0.43 to 0.41 mv/K. Thus, the cell should be in an isothermal section of the furnace. It is recommended that the temperature measuring leads be positioned halfway of the cell so as to reduce the effects of temperature gradient within a cell on the measured emf. In our case, a proportioning controller unit with a Pt/Pt-13% Rh thermocouple placed near the furnace windings was used to control the furnace temperature better than $\pm 0.5^\circ\text{C}$ over any run.

e. Influence of Electrical and Magnetic Fields on emf

Electrical and magnetic fields around the cell will affect the cell emf and add another source of emf to that actually determined by the electrodes. All the metallic portions of the experimental setup were grounded. To reduce the effect of the induced emf generated by the furnace windings, an inconel (Faraday shield) placed around the alumina tube (i.e., L in Figure I-13 (p. 34) and j in Figure I-14 (p. 37) was grounded.

CHAPTER IV

RESULTS

A. ELECTROLYTE

Electrolytes of composition ($\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$) made from 99.99% purity thorium nitrate and 99.9% purity yttrium nitrate powders gave the best results. Electrolytes after sintering were transparent and looked more or less like glass. They were quite brittle in nature. The lattice parameter of these electrolytes was found to be $5.5735 \text{ \AA}$ from x-ray diffraction pattern with $2\theta > 100^\circ$. Taking the lattice parameter of pure thoria and $\text{ThO}_2 + 10 \text{ mole\% } \text{Y}_2\text{O}_3$ as $5.60 \text{ \AA}$ (87) and $5.56 \text{ \AA}$ (86), respectively, and a linear variation of lattice parameter of YDT with mole% Y_2O_3 , $5.5735 \text{ \AA}$ corresponds to 6.625 mole% Y_2O_3 or 12.42 mole% $\text{YO}_{1.5}$. This composition corresponds to the maximum ionic conductivity region as shown in Figure I-10 (p. 21). In this case, there was no need for preheating at high temperature after sintering, because sintered electrolytes itself looked transparent. This shows that p_{O_2} was quite low in the sintering atmosphere and also the composition of these electrolytes correspond to maximum ionic conductivity (i.e., $t_{\text{ion}} = 1$). The trapping of electron holes by Y^{3+} ions leads to the formation of color centers at high oxygen pressures. Density was measured pycnometrically on these electrolytes. The density was observed to be 9.4043 gms/c.c. Assuming anion vacancy model, i.e. (the cation sublattice is completely filled by Th^{4+} and Y^{3+} ions and the

appropriate number of anion vacancies are created), the lattice parameter (a_0) and the composition of the electrolyte can be related to its density (d) by the formula:

$$d = [4X_1A_1 + 4X_2A_2 + 4(2X_1 + 1.5X_2)A_3]/a_0^3N \quad (1)$$

where X_1 and X_2 correspond to mole fractions of ThO_2 and $\text{YO}_{1.5}$, respectively; A_1 , A_2 and A_3 correspond to atomic weights of thorium, yttrium and oxygen, respectively, and N is Avogadro's number. Using Equation (1), the lattice parameter of $\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$ corresponds to a theoretical density of 9.4081 gms/c.c. Thus, the observed density of 9.4043 gms/c.c. corresponds to 99.96% of the theoretical density.

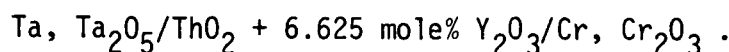
Electrolytes of composition ($\text{ThO}_2 + 9.2 \text{ mole\% } \text{Y}_2\text{O}_3$) made from 99.9% purity thorium and yttrium nitrate powders were light violet in color after sintering. But, heating the sintered pellets at 900°C at first in air and then in a flowing atmosphere of high purity argon for 24 hrs. turned the color of the electrolytes from light violet to white. These electrolytes were only 50% transparent and not brittle as the electrolytes of composition ($\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$). The lattice parameter of these electrolytes was found to be $5.5632 \text{ \AA}$. As before, taking the lattice parameter of pure thoria and $\text{ThO}_2 + 10 \text{ mole\% } \text{Y}_2\text{O}_3$ as $5.60 \text{ \AA}$ (87) and $5.56 \text{ \AA}$ (86), respectively, and a linear variation of lattice parameter of YDT with mole% Y_2O_3 , $5.5632 \text{ \AA}$ corresponds to 9.2 mole% Y_2O_3 or 16.85 mole% $\text{YO}_{1.5}$. The density of these electrolytes was pycnometrically observed to be 9.1711 gms./c.c. Using Equation (1), the theoretical density of these electrolytes is 9.2018 gms./c.c. Thus,

the observed density of 9.1711 gms./c.c. corresponds to 99.66% of the theoretical density. This proves the excellent agreement of the pycnometrically measured densities of fired pellets with those calculated for the anion vacancy model.

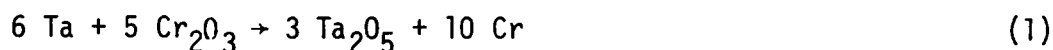
The electrolytes made directly by mixing the respective oxide powders were ivory white in color, and were not at all transparent.

B. PERFORMANCE OF THE CELL

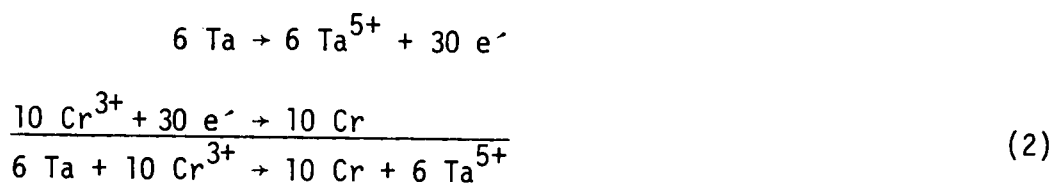
The emf cell under study here was:



This is a displacement type of cell and the cell reaction is:



or



Thus, this reaction involves a transfer of 30 electrons. Recalling from Equation (11) (p. 27), and assuming $t_{\text{ion}} = 1$, the standard free energy difference of Equation (1) is related to the emf developed across the cell by the equation:

$$\Delta G = 3(\Delta G_f^0(\text{Ta}_2\text{O}_5)) - 5(\Delta G_f^0(\text{Cr}_2\text{O}_3)) = -30*F*E. \quad (3)$$

The thermodynamics of the Cr-Cr₂O₃ equilibrium has been the subject of

numerous previous investigators (77,90-92). However, the results obtained by various techniques are in poor agreement. As seen from Equation (3), the calculated emf value will be very much sensitive to the value of $\Delta G_{f(\text{Cr}_2\text{O}_3)}^0$. In our present calculation, results of electrochemical technique incorporating ThO_2 -8 mole% Y_2O_3 electrolyte of Mazandarany et al. (77) for $\Delta G_{f(\text{Cr}_2\text{O}_3)}^0$ have been taken which are in close agreement with the gas equilibrium results of Jeanin et al. (90). The data of Mazandarany et al. (77) are in disagreement with the data of Pugliese et al. (92) and Tretjakow et al. (91). This disagreement may be due to the fact that the latter investigators have used calcia-stabilized zirconia as electrolytes which may have electronic conduction at very low oxygen potentials associated with $\text{Cr-Cr}_2\text{O}_3$ equilibrium ($\sim 10^{-23}$ atm. at 1000°C). $\Delta G_{f(\text{Ta}_2\text{O}_5)}^0$ has been taken from a review article by Rapp et al. (30). Thus, taking

$$\Delta G_{f(\text{Cr}_2\text{O}_3)}^0 = -266,600 + 59.78 T \text{ cal/mole} \quad (4)$$

$$\Delta G_{f(\text{Ta}_2\text{O}_5)}^0 = -481,000 + 98.50 T \text{ cal/mole} \quad (5)$$

and $F = 23,070$ cal/volt-equiv., the emf to be obtained at various temperatures has been calculated using Equation (3). The emf values from 750 - 1050°C at intervals of 50°C , are tabulated in Table I-2.

A total of six runs were made to study the performance of electrochemical cell. In each subsequent run, some modifications were made than the previous one, to study its effects on the performance of cell. Details regarding each run and results obtained are as follows:

TABLE I-2
CALCULATED EMFS AT VARIOUS TEMPERATURES FOR THE ELECTROCHEMICAL
CELL UNDER PRESENT STUDY

Temperature °K	Emf (E) (mv)
1023	163.96
1073	164.20
1123	164.45
1173	164.69
1223	164.94
1273	165.19
1323	165.43

RUN NO. 1: Here single chamber experimental setup (Figure I-13, p. 34); $\text{ThO}_2 + 9.2 \text{ mole\% } \text{Y}_2\text{O}_3$ as the electrolyte; high purity (99.995%) helium as the inert gas; Ta-Ta₂O₅ electrode sintered at 925°C for 1 day and Cr-Cr₂O₃ electrode sintered at 1100°C for 3 days were used. Initially, the emf of the cell was 10-20 mv at 1050°C. Maximum value of emf of 40.4 mv was obtained at this temperature after 4 days. The emf was not at all steady at this temperature (i.e., the fluctuation of the emf was more than $\pm 0.5 \text{ mv}$). After the run, the %wt. loss of Cr-Cr₂O₃ electrode was 1.6% and the %wt. gain of Ta-Ta₂O₅ electrode was 1.63%, which was quite significant.

RUN NO. 2: Here double chamber experimental setup (Figure I-14, p. 37) with the purification columns same as were in Run No. 1 was used. Apart from using $\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$ as the electrolyte, all other experimental variables were the same as in Run No. 1. The emf was negative at all temperatures and the minimum emf was -163.5 mv at 968°C when the resistance across the cell was found to be $5 \times 10^6 \text{ ohms}$. Finally, the emf increased to a value of -32.6 mv at 883°C, but the resistance across the cell at this temperature was ∞ . SEM analysis on the Cr-Cr₂O₃ electrode used after the run showed the presence of strong lines of Fe and very weak lines of Ca, Si and Al. Initial chromium metal powders too showed the presence of decisive peaks of Fe. At higher magnification of 500X, heterogeneous distribution of iron particles could be seen in initial chromium metal powders. Iron particles could even be separated by means of a magnet. Ta-Ta₂O₅ electrode and the electrolyte did not show presence of any undesirable elements. While starting the Run No. 3, it was found that the alumina tube had cracked.

The failure of this run may not solely be attributed to the oxygen leaks due to the crack in the tube, because cracks may have developed during the cooling of the furnace.

RUN NO. 3: In this run, high purity (99.995%) argon was used as the inert gas instead of helium. Double chamber experimental setup was used with a modified purification column consisting of copper turnings heated to a temperature of 400°C by means of a horizontal furnace. Electrodes which were sintered at 1400°C for a day in Oak Ridge National Laboratory were used in this run. Here the emf was positive but it steadily decreased to nearly 0 mv. At 698°C, the emf was 26.0 mv and at 774°C was 8.4 mv maximum. The emf finally dropped to 0.1 mv at 774°C in 36 hrs. Reason for this drop in emf was short circuiting of the cell by the layer of carbon formed on the periphery of electrolyte. This layer of carbon was formed by burning of bubbler medium (n-butylphthalate) which got sucked through when the cell was switched over to inert atmosphere at 200°C. Due to this layer, the resistance across the cell was found to be nearly 0 even at room temperature.

RUN NO. 4: All experimental variables were same as in Run No. 3; except that to prevent the flow of n-butylphthalate to the cell chambers, an empty bubbler was put before the actual bubbler. The emf was 166.0-167.0 mv at 970°C for 4 hrs. after 1-1/2 days. But, when the temperature was decreased to 905°C, the emf was quite unstable. The emf at this temperature of 905°C was 239.3 mv maximum after 3-1/2 days. Increase of flow rate in both the chambers caused a decrease in emf value by 100 mv at 905°C. But at 1045°C, there was not much of a flow rate effect on the cell emf. The emf at this temperature was 174.6 mv maximum. The emf was found to be very much sensitive to the contact

pressure, and this sensitivity of emf was proportional to the contact pressure. Whenever the temperature was raised, the emf dropped down at first, then started increasing steadily. The resistance across the cell was 7 K Ω and 4.5 K Ω at temperatures of 970° and 905°C, respectively. Whenever the cell was short circuited to measure the resistance, the emf is to drop sharply. But, it returned back to its original value within 5 minutes after the cell was open circuited again. After the run, only the Cr-Cr₂O₃ electrode was found very much oxidized.

RUN NO. 5: All experimental variables were the same as in Run No. 4; except that to improve the contact between the electrode and the electrolyte, some broken high purity alumina beads were put under the mullite tube k (Figure I-14, p. 37) in order to center the cell. At 895°C, the emf increased initially at a rate of 3.3 mv/hr. for the first 2 days; afterwards at a slower rate of 0.8 mv/hr. After 4 days, the emf at this temperature was 325.7 mv. The same trend of emf was observed at 1050°C too. The initial rate of increase of emf at this temperature was 4.2 mv/hr., a little higher than that observed at 895°C. The emf at this temperature increased to 321.7 mv after 6 days. A particular value of emf at this temperature did not remain constant for more than 7 hrs. Resistance of the cell at 895°C was found to be 15 K Ω . Emf was proportional to the flow rate of argon.

The Cr-Cr₂O₃ electrode was found to be quite oxidized after the run. X-ray diffractometer pattern on the face of this electrode which was in contact with the electrolyte showed the presence of Cr/Cr₂O₃ in a ratio of 1:2. There were also four extra strong lines and 8 weak lines on the x-ray diffraction pattern of this electrode, which could not be identified. An identical x-ray diffraction pattern was obtained

on the other face of this electrode in contact with the emf lead. Macroscopically, three different distinct regions could be seen on the surface of this electrode which was in contact with the electrolyte. These three regions could also be seen in macrostructure obtained by SEM as shown in Figure I-15. Portions B and D looked green in color under naked eyes and must then be Cr_2O_3 . Figure I-16 shows the portion B under higher magnification of 200X. Portions A and C in Figure I-15 looked grey under naked eyes; and the only difference between them is that the latter is coarser than the former. Figure I-17 shows the portion A under higher magnification of 200X. Lastly, portions E and F looked black in color under naked eyes and Figure I-18 shows the portion E under higher magnification of 200X. But chemical analysis on all these portions showed the presence of chromium only. Even by x-ray diffraction pattern, nothing positive could be detected about the undesirable products forming on the $\text{Cr-Cr}_2\text{O}_3$ electrode during the run. This surface oxide layer was thin. This layer was then polished off and x-ray diffraction pattern on this polished surface showed the presence of Cr and Cr_2O_3 only. This proves that only during the experimental run, some surface contamination has taken place.

RUN NO. 6: In this run, tantalum sleeves were put inside the inner chamber to reduce the oxidation of $\text{Cr-Cr}_2\text{O}_3$ electrode. A platinum o ring was also placed at the interface of $\text{Cr-Cr}_2\text{O}_3$ electrode and the electrolyte to reduce the effect of mixed potential. Here $\text{Ta-Ta}_2\text{O}_5$ electrode sintered at 925°C for a day was used, because x-ray diffraction pattern of electrodes sintered at Oak Ridge National Laboratory at 1400°C for a day in an argon atmosphere showed the

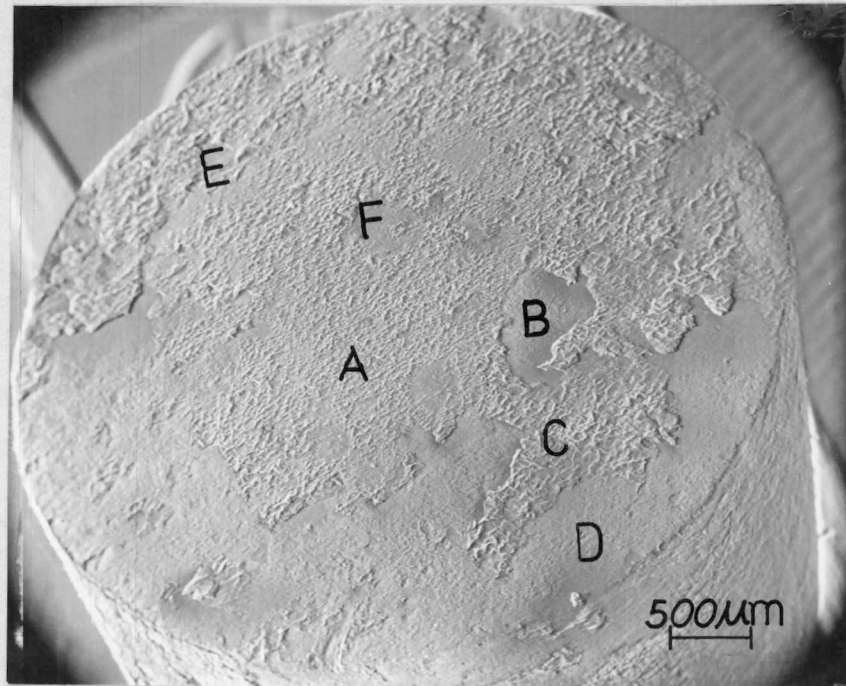


Figure I-15. SEM photomicrograph of the face of Cr-Cr₂O₃ electrode in contact with the electrolyte after Run No. 6.

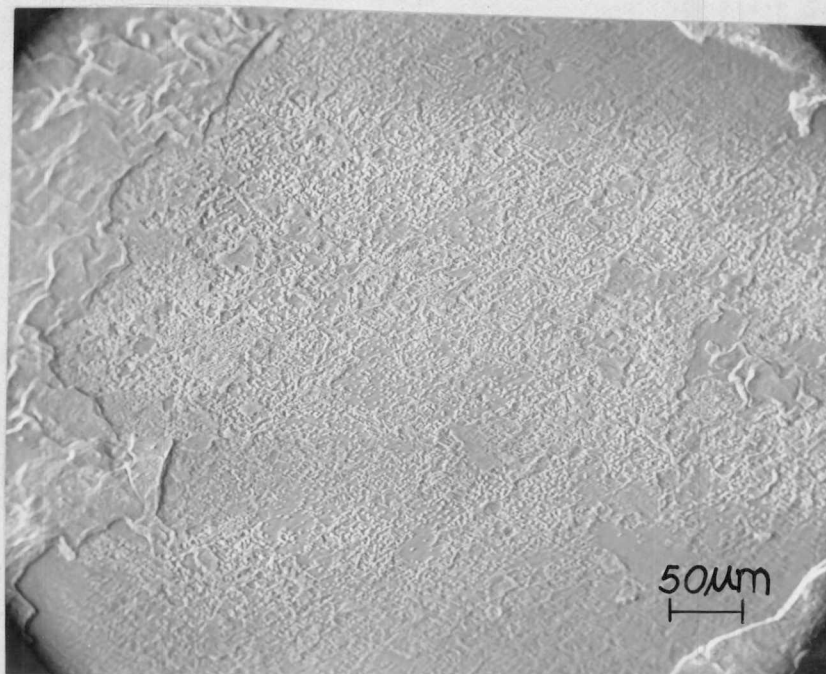


Figure I-16. SEM photomicrograph of portion B of Figure I-15.

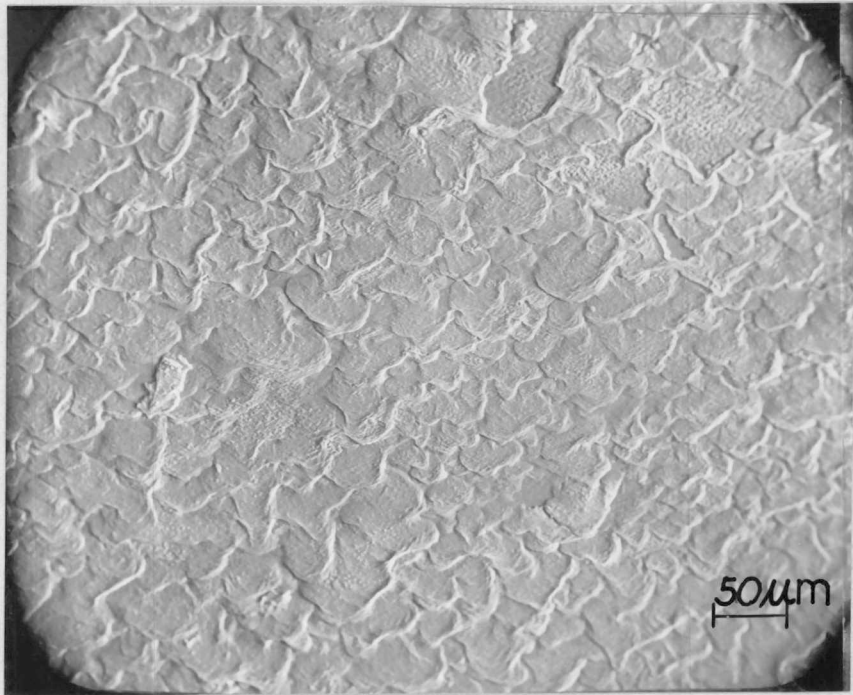


Figure I-17. SEM photomicrograph of portion A of Figure I-15.

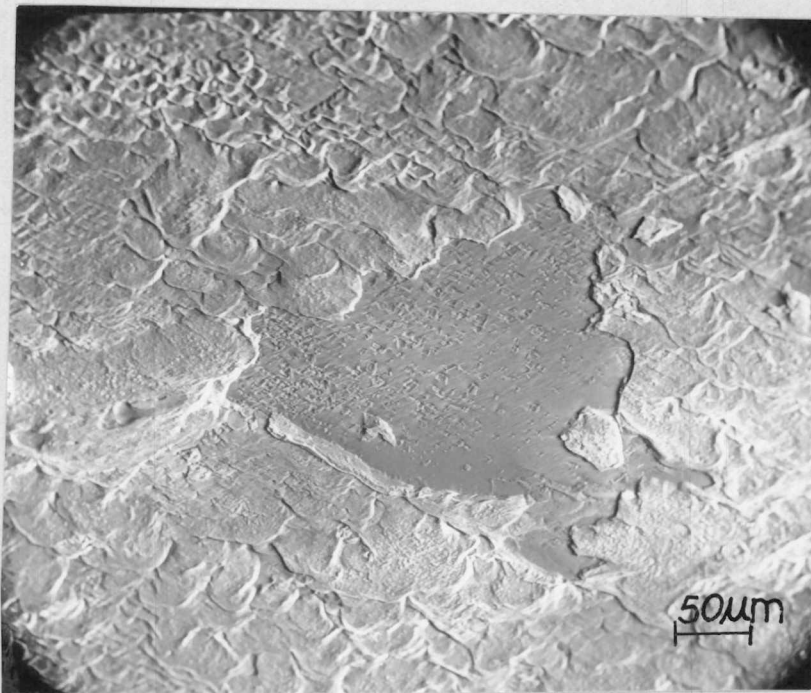


Figure I-18. SEM photomicrograph of portion E of Figure I-15.

presence of some extra lines, which could not be identified. All other experimental variables were the same as in Run No. 5.

The emf at 893°C was 180.9 mv after 4 days. Resistance across the cell at this temperature was 5 K Ω . But emf steadily increased to a value of 569.2 mv in 24 hrs. and then the emf continued to increase at a rate of 5 mv/day. When the temperature was increased to 1032°C, the emf was 554.4 mv after 24 hrs. An increase in the flow rate of the gas in both the chambers at this temperature resulted in a sharp increase of emf by 100 mv within 5 mins. The opposite effect was seen on decreasing the flow rate. But this time, the decrease in emf was 50 mv in 5 mins. When the flow of the gas was stopped completely in both the chambers, emf started decreasing. There was no effect of contact pressure on emf.

X-ray diffraction pattern of the face of Cr-Cr₂O₃ electrode, which was in contact with the electrolyte, showed the presence of Cr/Cr₂O₃ in a ratio of 3:2. Extra lines were found on its diffraction pattern which were almost identical to the ones obtained in the case of Run No. 5. Macroscopically, the electrode looked less oxidized than the electrode of Run No. 5. Tantalum sleeves, which were put inside the inner chamber, were heavily oxidized. They turned into a white powder, indicating the formation of Ta₂O₅. But, the tantalum foils placed upstream and in the vicinity of the outer chamber looked good. X-ray diffraction pattern of the face of Ta-Ta₂O₅ electrode in contact with the electrolyte showed the presence of Ta/Ta₂O₅ in a ratio of 5:1. Apart from the lines β -Ta₂O₅, some extra lines were found on its diffraction pattern which were quite identical to the ones found in the case of this electrode sintered at ORNL. The portion of the face which

was not in contact with the electrolyte was only oxidized. White specks of Ta_2O_5 could be seen on the oxidized portion of the electrode.

CHAPTER V

DISCUSSION

A. ELECTROLYTE

Since the particle size distribution of the starting oxide powder greatly influences the sintering behavior of the oxide, fine grained oxides are advantageous. Our newly developed nitrate process has yielded a density of 99.96% of theoretical density in the case of the $\text{ThO}_2 + 6.625 \text{ mole\% } \text{Y}_2\text{O}_3$ electrolytes. This high density of the sintered electrolytes proves the fact that by coprecipitation of solid solution powders of YDT, finer particle size distribution can be obtained than by directly mixing the commercial respective oxide powders. Previous studies (86,88) indicate that the oxalate method yielded the maximum density. The oxalate method involves at first filtration and dehydration of the precipitate obtained by adding saturated oxalic acid drop by drop to the ice cold nitrate solutions, and finally calcining the dehydrated precipitate at 900°C . But, our nitrate process is less complicated and not much grinding of the precipitated solid solution powders was necessary. The powders could easily be sieved through -325 mesh sieve.

As it has been seen before (42,86,89), in our case too, pycnometrically measured densities of fired pellets have agreed well with those calculated for the anion vacancy model. This observation confirms the fact that when the Th^{4+} ions are replaced by Y^{3+} ions, charge neutrality is restored by complete filling of cation sublattice by Th^{4+} and Y^{3+} ions and the creation of appropriate number of anion

vacancies. Also, the ionic conductivity of YDT increases with the increase in mole% of Y_2O_3 due to the increase in creation of number of anion vacancies.

The decisive material parameter determining the magnitude of the electronic conductivity in an electrolyte is the electronic band gap (B), which should be larger than $T/300$ eV (19) for good solid electrolytes. This band gap also determines the position of the optical absorption edge, whose value can be obtained from optical measurements. Transparent electrolytes correspond to minimum absorption edge and hence the maximum electronic band gap. So, our electrolytes of composition $ThO_2 + 6.625$ mole% Y_2O_3 may well be assumed having $t_{ion} \approx 1$ due to its transparent color. The light violet color obtained in the case of $ThO_2 + 9.2$ mole% Y_2O_3 electrolytes may be due to the excessive doping by yttria or using less purity (99.9%) thorium nitrate powders. As seen from Figure I-10 (p. 21), doping in excess of 9-13 mole% $YO_{1.5}$ causes a decrease in ionic conductivity due to vacancy ordering (14) or vacancy clustering (15). This may be one of the important reasons for the failure of the operation of cell studied here using $ThO_2 + 9.2$ mole% Y_2O_3 as the electrolyte. Subbarao et al. (86) obtained the color of the electrolytes made by the oxalate method, ranging from ivory white to brown; the intensity of brown color increasing with $YO_{1.5}$ at a given temperature. So, on the basis of the relation between the color of the electrolyte and the electronic band gap, it is quite questionable whether they (86) could obtain the ideal electrolytes, i.e., $t_{ion} \approx 1$ by the oxalate method. Direct mixing of the respective oxide powders yielded white electrolyte pellets (77) as was obtained in our case.

Tsai (93) studied the cell: $\text{MO}, \text{MoO}_2/\text{YDT}/\text{FeO}, \text{Fe}_3\text{O}_4$, where electrolytes were fabricated by our nitrate process. The observed cell emfs were found to be in excellent agreement with the calculated values.

On the basis of the above discussion, it can be well argued that our nitrate process may be the best fabrication method for YDT electrolytes.

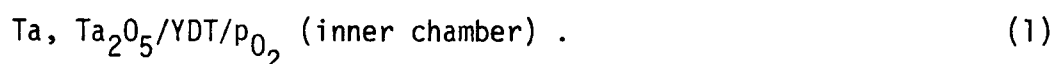
B. PERFORMANCE OF THE CELL

The failure of the Run No. 1 may be attributed to the electronic conduction in the electrolyte. As seen from Figure I-10 (p. 21), when thoria is doped with greater than 9-13 mole% $\text{YO}_{1.5}$, t_{ion} is no more equal to 1 due to the vacancy ordering or vacancy clustering. This phenomenon of vacancy ordering or vacancy clustering generates electronic defects for the charge neutrality. In this run, the electrolyte was of composition >13 mole% $\text{YO}_{1.5}$ (i.e., 16.85 mole% $\text{YO}_{1.5}$). The weight loss and gain measurements on these electrodes after the run furthermore confirms this fact of electronic conduction, due to which there is weight gain at $\text{Ta-Ta}_2\text{O}_5$ electrode by the transport of oxygen ions to $\text{Ta-Ta}_2\text{O}_5$ electrode, countercurrent to the electron flow.

The equilibrium partial pressure of oxygen in the case of $\text{Cr-Cr}_2\text{O}_3$ and $\text{Ta-Ta}_2\text{O}_5$ electrode is 10^{-23} and 10^{-25} atm., respectively, at 1000°C . So, the performance of electrochemical cell involving these electrodes depends very much on the partial pressure of oxygen in the environment of cell. Previous thermodynamic measurements (13,77,85) at this low value of p_{O_2} indicate the better purification units for the primary deoxidizing of the gas than the copper turnings heated to 400°C as in

our present study. For example, Worrell et al. (13) have used Zr-Ti alloy (87.5 at. % Zr) chips at 375°C, whereas Mazandarany et al. (77) have used $\text{Mg}(\text{ClO}_4)_2$ and activated CuO (BTS catalyst) as primary deoxidizing agents. As was pointed out in Section C(a) (Chapter III), Heshmatpour et al. (85) could purify argon to as low as 10^{-25} atm. of argon. Heavily oxidized Cr-Cr₂O₃ electrodes in Run Nos. 4, 5, and 6 indicate that p_{O_2} in the inner chamber was not low. Complete oxidation of Ta sleeves into white Ta₂O₅ powder in Run No. 6 indicates particularly that the environment of inner chamber was not very reducing one. This may have been caused by the use of tygon tubing e (Figure I-14, p. 37) through which the gas for the inner chamber passes. Tantalum foils placed upstream and in the vicinity of the outer chamber and also Ta-Ta₂O₅ electrode did not oxidize heavily, indicating that the inert gas may be picking up some oxygen on its way to the inner chamber by the diffusion of molecular oxygen from the atmosphere through the tygon tubing. Recalling that, in Run No. 6, after the run Ta/Ta₂O₅ was 5:1, whereas Cr/Cr₂O₃ 3:2, although initially both these electrodes were made by mixing respective metal:oxide in the ratio 10:1. Actually, Ta-Ta₂O₅ electrode should get preferentially more oxidized than Cr-Cr₂O₃, because thermodynamically Ta₂O₅ is more stable than Cr-Cr₂O₃. This fact furthermore confirms that the environment in the inner chamber was certainly less reducing than that in the outside chamber.

The high emf values obtained in Run Nos. 4, 5, and 6 may be due to the formation of this cell:



Here the cell reaction becomes,



$$\Delta G_R = \Delta G_f^0 (\text{Ta}_2\text{O}_5) - 5/2 RT \ln p_{\text{O}_2} = -10 EF \quad (3)$$

$$E = \frac{RT}{10F} \ln \frac{p_{\text{O}_2}^{5/2} (\text{inner chamber})}{p_{\text{O}_2}^e} \quad (4)$$

where $p_{\text{O}_2}^e$ is the equilibrium partial pressure of Ta to form Ta_2O_5 , which is equal to 10^{-25} at 1000°C . Using Equation (4), a p_{O_2} (inner chamber) of 10^{-4} atm. will give rise to cell emf of 380 mv. Thus, the observations in Run Nos. 4, 5, and 6 of the increase of emf with time indicate that after a layer of oxide has formed on the $\text{Cr-Cr}_2\text{O}_3$ electrode; the cell under consideration is no more operative. The preferential oxidation of the $\text{Cr-Cr}_2\text{O}_3$ electrode is based on the arguments given in the preceding paragraph. Thus, the cell discussed above, i.e. (1) instead becomes operative and emf increases according to the partial pressure of oxygen established in the inner chamber. This emf will be very much dependent on the clearance between $\text{Cr-Cr}_2\text{O}_3$ electrode and the inner diameter of the mullite tube k (Figure I-14, p. 37). The same reason can be attributed to the flow rate effect on emf. As the flow rate in the inner chamber (i.e., p_{O_2} (inner chamber)) increases, thereby the emf increases and just the opposite to this with the decrease in flow rate in the inner chamber. This phenomenon was particularly observed in the case of Run Nos. 5 and 6. In fact, Pugliese et al. (92) have determined the free energy of formation of Cr_2O_3 using the cell (1) discussed here.

Taking σ_{ion} of $\text{ThO}_2(\text{Y}_2\text{O}_3)$ from Figure I-10 (p. 21) as $2.45 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1000°C , an electrolyte of $0.35 \text{ cm } \phi \times 0.4 \text{ cm}$

should have a resistance of about 500Ω at 1000°C . Of course, the resistance of the cell will be higher than this, in case there is poor contact between the electrode and electrolyte. The high resistance of the order of Kilo-ohms which has been observed in our various runs indicates that either there is poor contact between the electrode and electrolyte or oxidation of the electrodes has occurred.

With two-phase electrodes such as metal-metal oxide mixtures, equilibration times are limited by diffusional processes in the metal or the oxide. There also may be equilibration difficulties caused by the formation of a coherent oxide coating around the metal or alloy particle in the electrode. A long equilibration time has been reported in the case of cell having Nb-NbO and Ta-Ta₂O₅ as electrodes (13). So, it is quite expected that the present cell under study may have long equilibration times.

Thus, it may be concluded on the basis of the above discussions, that the failure of satisfactory performance of the cell is due to the improper environment around the cell. If an electrolyte can sustain an emf of 550 mv as was observed in Run No. 6, the electrolyte fabricated by our newly developed nitrate process is surely the best method of fabrication for the YDT electrolytes.

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PART II: CALCULATION OF THE Fe-Ni PHASE DIAGRAM
FROM 1184°K TO 300°K

CHAPTER I

INTRODUCTION

Superalloys are nickel-, iron-, or cobalt-base alloys which have excellent corrosion and oxidation resistance and strength in high temperature systems such as jet aircraft engines and gas turbines. Nickel-base superalloys are the most important because of their favorable high temperature mechanical properties, combined with excellent corrosion resistance in aqueous media and oxidation resistance at high temperatures. Hastelloy alloy G and Hastelloy alloy X are typical nickel-base superalloys containing 15-20% Fe. These superalloys find wide applications in jet engine sheet parts and as excellent pitting and stress corrosion cracking resistant materials.

Several studies exist on the role of Fe in nickel-base superalloys. With regard to the solid solution strengthening, Fe strengthens only slightly due to its mere 0.3% difference in atomic diameter from nickel. But the amount of γ' is increased by the addition of Fe, and the high temperature creep strength in superalloys is very much dictated by the amount of γ' present. For the best strengthening of the structure by the γ' precipitates, it is desired to have high antiphase boundary energy, which iron increases. There is evidence that this might be the most important factor impeding the movement of the dislocations through a matrix containing γ' particles. Also, it has been reported (58) that iron decreases the coarsening rate of γ' in nickel-base superalloys.

Examination of the literature (1,2) on the iron-nickel system indicates that the available phase diagrams for the solid state region, particularly below 500°C, are inadequate. This is because most transformations in this system are often extremely sluggish, with the result that attempts to establish equilibrium by classical anneal methods using specimens from massive alloys are laborious and generally fall short of yielding equilibrium. Iron meteorites, composed of iron-nickel alloys containing only small amounts of other elements, have played an important role in the study of the Fe-Ni phase diagram, because these have been cooled at approximately 1°C per 10^6 year (3).

Via computer techniques, estimates of low temperature phase equilibria can be made using high temperature thermodynamic data where equilibrium is easily achieved. Using computer programs available in this Department,* various sources of solution thermochemistry information at high temperatures for Ni-Fe alloys have been analyzed in order to determine the best fit with the most recent experimental α - γ boundary study of Romig et al. (13). Also, the γ -Ni₃Fe and α -Ni₃Fe boundaries have been determined graphically based on the pulse calorimetric measurements of C_p and the heat of the order-disorder transformation for the Ni₃Fe** alloy by Kollie et al. (14).

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**Ni₃Fe refers to 75 at. % Ni + 25 at. % Fe alloy only; neither its order nor disorder state.

CHAPTER II

LITERATURE SURVEY

A. STUDY OF THE Fe-Ni PHASE DIAGRAM

The most recent evaluation of the Fe-Ni phase diagram is that of Shunk (2) as shown in Figure II-1. The phase diagram for the solid state region below 500°C is inadequate still today due to the difficulty in attaining equilibrium in sluggish transformations occurring in this system. Precipitation of α -Fe from γ is extremely slow; a martensitic b.c.c. phase (supersaturated α -Fe) is apt to form even on relatively slow cooling. Iron meteorites, having Ni contents ranging from 4 to 42%, play an important role in the study of the iron-nickel phase diagram. This is due to the fact that most meteorites have cooled with a rate of 1°C per 10^6 year (3). Most of the iron meteorites belong to the so-called octahedrites, which are composed mainly of two phases: kamacite, which has b.c.c. structure (called ferrite or α -phase) and taenite, with f.c.c. structure (austenite or γ -phase). The (γ -Fe,Ni) decomposes eutectoidally at 618°K, 52% Ni as shown in Figure II-1. This eutectoidal decomposition is based on the observations made on alloys which were prepared as thin films by concurrent decomposition of Ni and Fe carbonyls (33). Using electron microprobe and scanning electron microscope techniques, Romig et al. (13) have recently determined the α - γ boundary.

Firm evidence for atomic ordering of the cubic, Cu_3Au -type occurs in f.c.c. alloys at about the stoichiometric composition Ni_3Fe

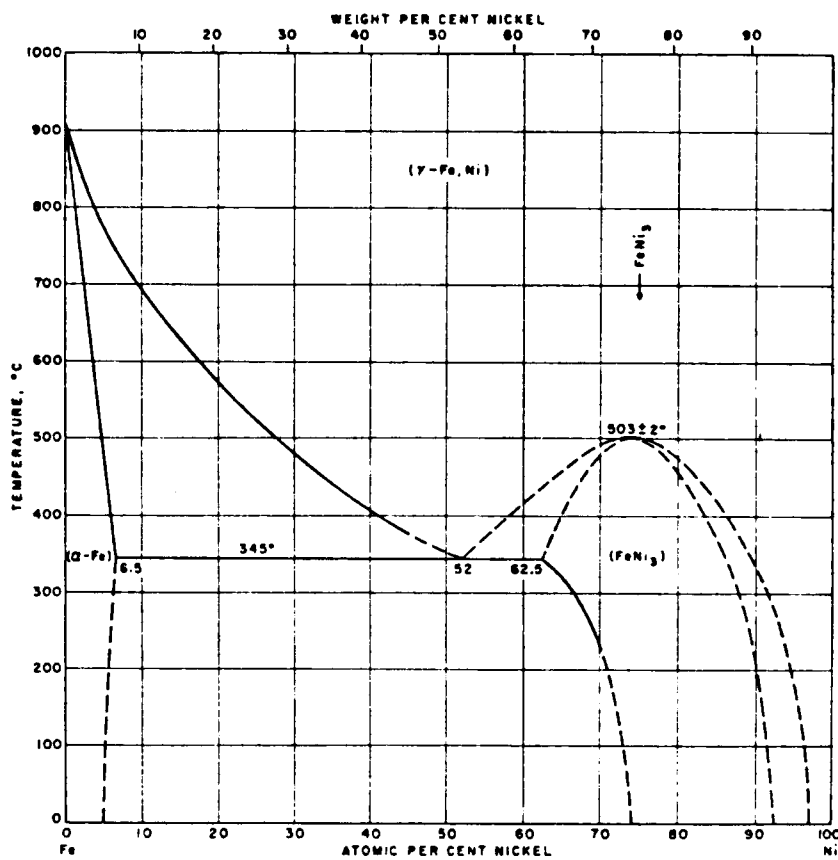


Figure II-1. Fe-Ni phase diagram according to Shunk (2).

at temperatures near 500°C (4-6). F.c.c. alloys of composition NiFe, when subjected to neutron (7) or electron (8) irradiation and simultaneously to a magnetic field, developed a tetragonal CuAu type order, the largest effect (with neutrons) taking place at about 300°C. Recent study in taenites has shown that they decompose into an ordered phase with L10 structure and a disordered f.c.c. iron-nickel alloy containing less than 25% Ni at temperatures below 300°C (9). The two phases have the same bravais lattice; i.e., they form a pseudo monocrystal. The first TEM evidence (both electron diffraction patterns and centered dark field (CDF) images) for FeNi in clear taenite has been reported recently (59). Based on the above information, various modified Fe-Ni phase diagrams have been suggested (26,60,61). The one of Fe-Ni of Ono et al. (61) is shown in Figure II-2.

Numerous studies exist on the measurement of only high temperature thermodynamic properties of the Fe-Ni system. Based on these high temperature thermodynamic data and using computer techniques the α - γ boundary has been calculated in the present work. Also, the γ -Ni₃Fe and α -Ni₃Fe boundaries have been determined graphically based on the pulse calorimetric measurements of C_p and the heat of the order-disorder transformation for the disordered Ni₃Fe by Kollie et al. (14).

B. THERMODYNAMIC PROPERTIES OF THE Fe-Ni ALLOYS

Heat of Mixing of γ Alloys (ΔH_Y^M)

The heat of mixing (ΔH_Y^M) data are summarized in Figure II-3. The heat of mixing is negative. The data of (17,20) shows genuine

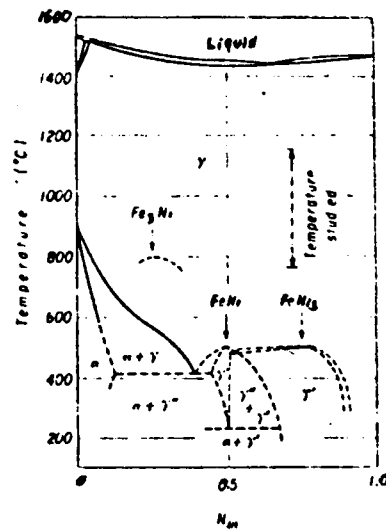


Figure II-2. Proposed Fe-Ni phase diagram of Ono et al. (61).

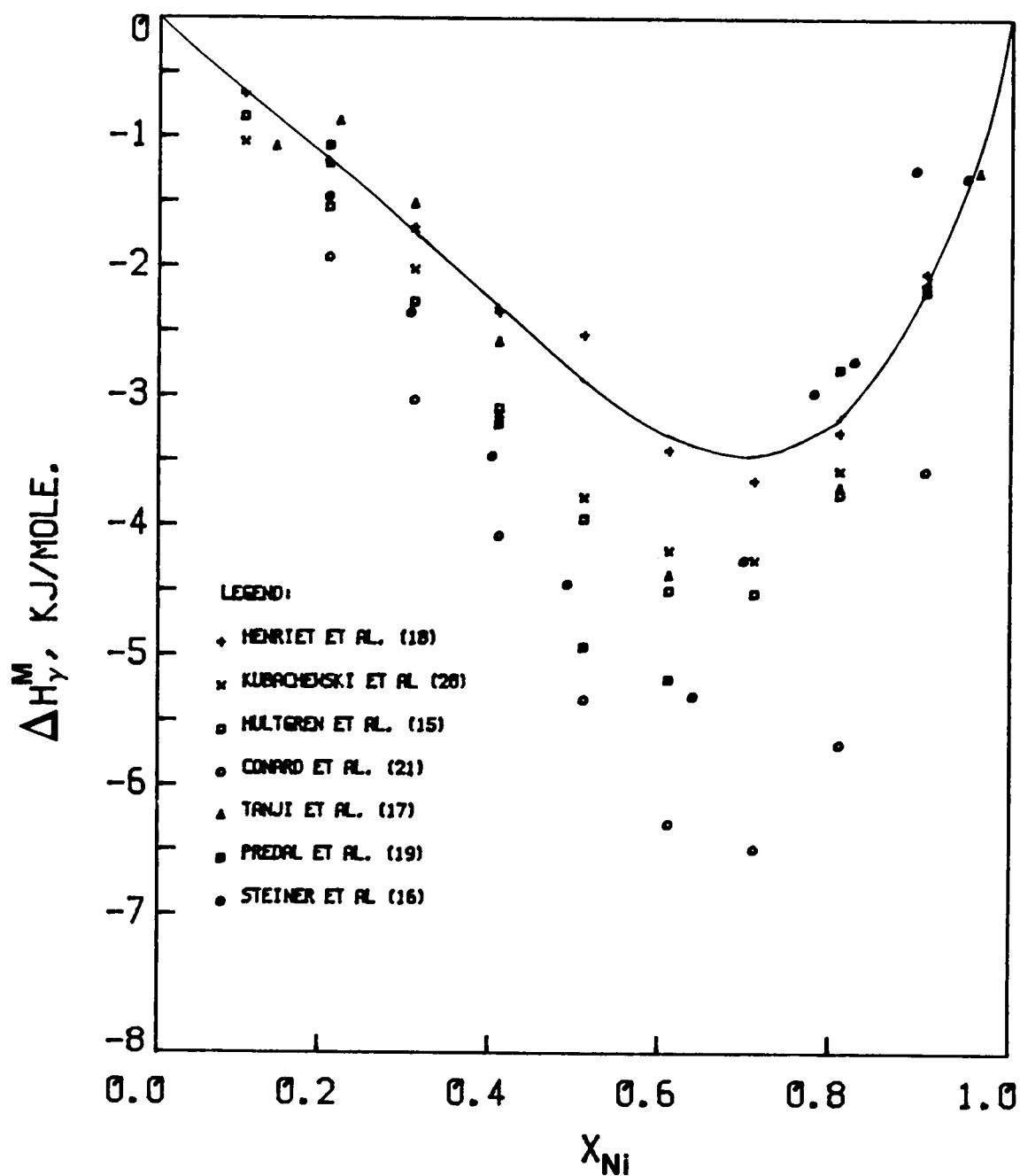


Figure II-3. Comparison of $\Delta H_{\gamma}^M(S)$ results. Solid curve is the representation of Henri et al. (18) data fitted to a second order Legendre polynomial to be discussed in Chapter III, Section A.

irregularity at about 20 at. % Ni and that the alloy must split into two f.c.c. phases in the equilibrium state at sufficiently low temperatures, unless the splitting is suppressed by the mixing entropy effect. This tendency to immiscibility in Fe-Ni (f.c.c.) system has also been reported in the experimental works of Albertsen et al. (9) and Ananthanarayanan et al. (26) and may closely be related to the so-called Invar problem. For example, Young's modulus and shear modulus versus concentration curves in the paramagnetic state show a minimum near the invar region (40 to 50 at. % Ni) (28). This tendency to immiscibility in Fe-Ni (f.c.c.) seems to prove that ΔH_Y^M is less negative than the data available at present which have been summarized in Figure II-3. So, for our present calculation, the least negative data reported to this date, those of Henriët et al. (18), have been used.

Free Energy of Mixing of γ Alloys (ΔG_Y^F)

A number of determinations of ΔG_Y^F have been made on solid (Ni-Fe, γ) alloys (17,18, 21-24) using various techniques mainly in the range of 1000-1400°K as shown in Figure II-4. The data of ΔG_Y^F obtained by using solid electrolyte emf techniques (17,18,23) are in considerable disagreement with those obtained by other techniques. This is attributed (27) to the nonequilibrium conditions caused by sluggish diffusion rates in the oxide spinel phase, which coexists with the alloy for compositions rich in nickel. But, solid electrolyte emf techniques give an uncertainty of only 400J corresponding to 1 mv difference in the cell voltage as compared to 2000J obtained by the method of equilibrium of the alloy with a suitable vapor phase. The

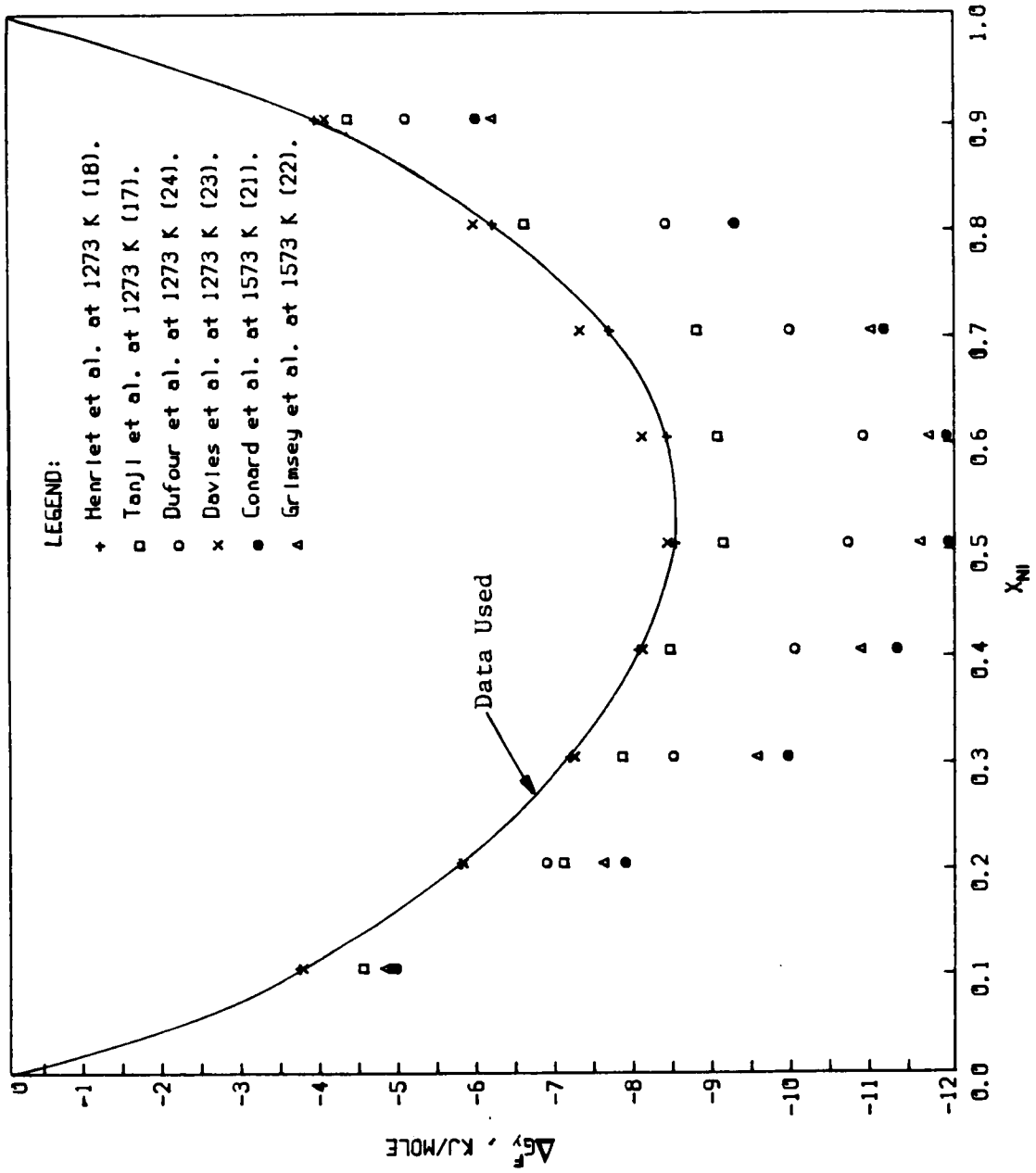


Figure II-4. Comparison of $\Delta G^\circ_F(S)$ results.

deviation from ideality is negative in all cases. The present calculation uses the data of Henriot et al. (18) where the results show that iron obeys Raoult's law to within narrow limits between $X_{Fe} = 1$ and $X_{Fe} = 0.5$, after which it shows a negative deviation.

Specific Heats of Fe-Ni Alloys at High Temperatures

Few studies (5,14,28,29) exist of the systematic investigations of the specific heat of Fe-Ni alloys at high temperatures. Kaya et al. (29) have only studied the alloys with more than 50% Ni. The pulse calorimetric measurements of Kollie et al. (14) give values for the disordered Ni_3Fe . It is difficult to prevent ordering below 782°K. Tanji et al. (28) found that a heating rate of 1-2°K/min was insufficient to prevent ordering; thus they were not able to obtain C_p data for the disordered alloy. But Kollie et al. (14) used a pulse calorimeter in which the sufficiently high heating rate of 60°K/sec permitted them to measure the heat capacity of disordered Ni_3Fe between 300 and 1670°K, suppressing long-range ordering below 782°K. The heat of transformation was found to be 3680 ± 140 Joules/mole and the temperature of transformation at 773°K. This value of the heat of transformation is in good agreement with the value of 3450 Joules/mole obtained by Leech et al. (5). C_p data available at present are found to be in good agreement with each other as shown in the case of Ni_3Fe in Figure II-5. The curve from Tanji et al. (28) in Figure II-5 has two peaks; one at a higher temperature corresponding to the Curie temperature, T_C , and another at a lower temperature due to Ni_3Fe ordering suggesting that they could not prevent ordering below 782°K. No measurements on the specific heat of ordered FeNi has been reported in the literature.

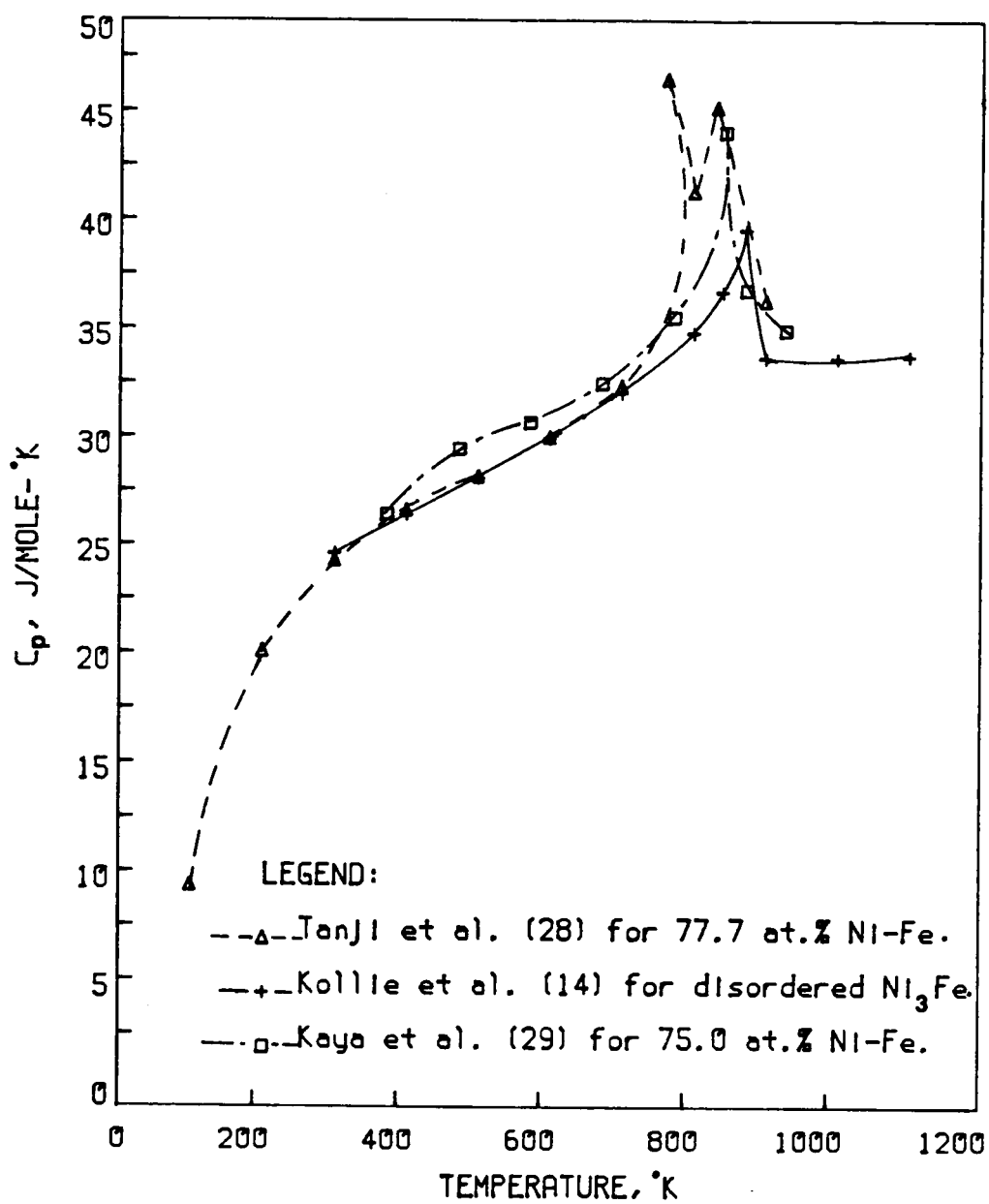


Figure II-5. Comparison of C_p data of Ni_3Fe .

C. CALCULATIONS OF EQUILIBRIUM PHASE DIAGRAMS

Hillert (36) has provided a lucid account of the advantages which would accrue to the studies of phase equilibria if thermodynamic data and the phase diagram information were combined via computer techniques. The approach is to use enthalpies and free energies of the stable phases in a system which have been determined under conditions where equilibrium is easily achieved. This information is then used for the calculation of phase boundaries under conditions where chemical equilibration is hampered by kinetic factors, i.e., at low temperature. Inaccuracies in determination of miscibility gaps, solubilities in the solid state, and solidus curves are typical examples of the shortcomings of direct experimental determination of equilibrium diagrams. Integration of thermochemical and phase diagram data provide a superior means of predicting accurate phase boundaries.

Current methods of phase diagram computation start with measured activity data. Here, experimental thermodynamic measurements are reduced to mathematical description with the aid of series representations or graphical smoothing of tabular data and are combined with the best available phase diagram data to calculate a "best" phase diagram. Kubachewski and co-workers (37-44) have used this technique to calculate equilibrium for thirty systems.

The bond structure of metallic phases is so complex and so little understood that no well-founded theoretical form for the free

energy function is known. Thus, it is necessary to resort to convenient mathematical forms. The general, well-known expression for the free energy of a phase as a function of temperature and composition is given by Hillert (36). The main problem in using this free energy function lies in the expression of excess free energy of formation as a function of temperature and composition. In the regular solution model, the excess free energy of formation (ΔG^{XS}) is identical with the heat of formation (ΔH^F) and is expressed as

$$\Delta G^{XS} = \alpha' X_A X_B \quad (1)$$

where X_A and X_B are the mole fractions of the components of metals A and B and α' is the temperature and composition independent interaction parameter and signifies the net gain or loss in the bond energy. A positive value of α' signifies like bonds are stronger than unlike bonds; this leads to the formation of a miscibility gap. A negative value of α' signifies just the reverse and leads to compound formation. α' is zero in the case of an ideal solution. Here the entropy of mixing has approximately the Raoult's law value. This is a relatively simple expression for the excess free energy as defined by regular solution model; but it is valid only for a very limited number of actual solutions. Another commonly used model is the subregular solution model which takes into account the composition dependence of α' . ΔG^{XS} is expressed as

$$\Delta G^{XS} = [a + b \cdot X] \cdot X_A \cdot X_B \quad (2)$$

where $\alpha' = a+b \cdot X$ and a and b are constants. However, it is often very difficult to formulate the excess quantity according to a sound physical model of the solution and it is thus very common simply to apply some power series expression, which of course must be formulated in such a way that it goes to zero for the pure elements. ΔG^{XS} has commonly been expressed in the form of a Legendre polynomial (21,62):

$$\Delta G^{XS} = X_A X_B [A + B(1 - 2X_A) + C(1 - 2X_A)^2 + \dots] - T[D + E(1 - 2X_A) + F(1 - 2X_A)^2 + \dots] \quad (3)$$

Thurmond and co-workers (45-47) and Panish (48) have coupled thermochemical data and a regular solution representation to calculate phase diagrams for binary and ternary systems. Wriedt (49) and Williams (50) expanded the subregular model to include higher order compositional terms as well as the temperature dependent effects.

The graphical method of equilibrium diagram evaluation is convenient and simple for binary systems that are not too complicated. However, it appears that the evaluation of phase boundaries at lower temperatures from thermodynamic data is so superior to the various conventional experimental methods that it should usefully be extended to more complicated binary, ternary and multicomponent systems. For these, the graphical method is quite inadequate with respect to the accuracy in the determination of phase boundaries and computer methods must be used. Moreover, computer methods aid in the evaluation of phase boundaries of more complicated systems where the first derivative of free energy functions, usually second or higher order polynomials, cannot be

solved without the aid of computer methods. Computer programs to determine miscibility gaps and the boundaries of solid solution phases from the free energy data exist in this Department as well.

Work is currently being done on the calculation of equilibrium diagrams on the basis of lattice stability of compounds and interaction parameters, as enumerated by Van Laar (51). By this method, systems for which few data exist can be investigated as little thermodynamic data are required. The main problem with this approach is to estimate input parameters which have validity for the real system under consideration. Estimation of regular solution parameters on a physical basis has been attempted by Kaufman (52). Calculation of the relative energies of the principal structures of the pure metal (i.e., the lattice stability at 0°K) has been attempted (52-57) based on the application of pseudo potential theory.

Only a few studies exist in the literature (10-12) on the determination of phase boundaries of the Fe-Ni system at low temperatures using the high temperature thermodynamic data available. Using the computer program available in this Department, various sources of solution thermochemistry information at high temperatures have been analyzed, in order to obtain the best fit with the most recent experimental α - γ boundary study of Romig et al. (13). Also, the γ -Ni₃Fe and α -Ni₃Fe boundaries have been calculated graphically.

CHAPTER III

DETERMINATION OF PHASE BOUNDARIES

A. MODEL FOR SOLID ALLOYS

Previous subregular models were employed (12,25) for describing the Fe-Ni system based on available measured thermodynamic properties. Conard et al. (21) derived an empirical subregular solution model by fitting $\Delta G_Y^{XS}/RT$ to a Legendre polynomial model. In our calculation, assessed values of the excess enthalpies and entropies of formation (usually assumed to be temperature-independent) of the γ phase are represented by ΔG_Y^{XS} equation in the form of Legendre polynomial:

$$\Delta G_Y^{XS} = X_{Ni} X_{Fe} [\{ A + B(1 - 2X_{Ni}) + C(1 - 2X_{Ni})^2 \} - T \{ D + E(1 - 2X_{Ni}) \}] \quad (1)$$

where X_{Ni} and X_{Fe} correspond to the mole fraction of Ni and Fe, respectively, and A, B, C. . . . are constants. The first term in Equation (1) is nothing but the heat of mixing where third and higher order terms were found to be unnecessary. The data of heat of mixing by Henriot et al. (18) have been fitted to a second order Legendre polynomial using least square program. The second term in Equation (1) is the excess entropy of formation (ΔS_Y^{XS}). First, the integral entropies of formation (ΔS_Y^F) were determined from the slope of ΔG_Y^F vs. temperature curves of Henriot et al. (18) for the entire composition range of alloys. ΔG_Y^F vs. X_{Ni} at different temperatures from their data is shown in

Figure II-6. Next, ΔS_Y^{XS} was calculated for each of the alloys by the equation:

$$\Delta S_Y^{XS} = \Delta S_Y - \Delta S_Y^{ideal} \quad (2)$$

$$= \Delta S_Y + R[X_{Ni} \ln(X_{Ni}) + (1 - X_{Ni}) \ln(1 - X_{Ni})] \quad (3)$$

ΔS_Y^{XS} was then fitted to a first order Legendre polynomial using least square program. Thus, the free energy of formation of γ phase as a function of temperature and composition can be described by the expression:

$$\begin{aligned} \Delta G_Y^F = & RT[X_{Ni} \ln X_{Ni} + (1 - X_{Ni}) \ln (1 - X_{Ni})] \\ & + X_{Ni}(1 - X_{Ni})[A + B(1 - 2X_{Ni}) + C(1 - 2X_{Ni})^2] \\ & - T\{D + E(1 - 2X_{Ni})\} \end{aligned} \quad (4)$$

where the first term defines the ideal term and the f.c.c. state for pure Fe and Ni has been taken as the standard state.

Due to the lack of reliable thermodynamic data on α alloys, they have been assumed to be ideal. Thus the free energy of formation of α phase with respect to pure b.c.c. Fe and Ni as the standard state can be expressed as:

$$\Delta G_\alpha^F = RT[X_{Ni} \ln X_{Ni} + (1 - X_{Ni}) \ln (1 - X_{Ni})] \quad (5)$$

It is advantageous to choose standard states that do not undergo any drastic changes in the range of temperature concerned. It would be

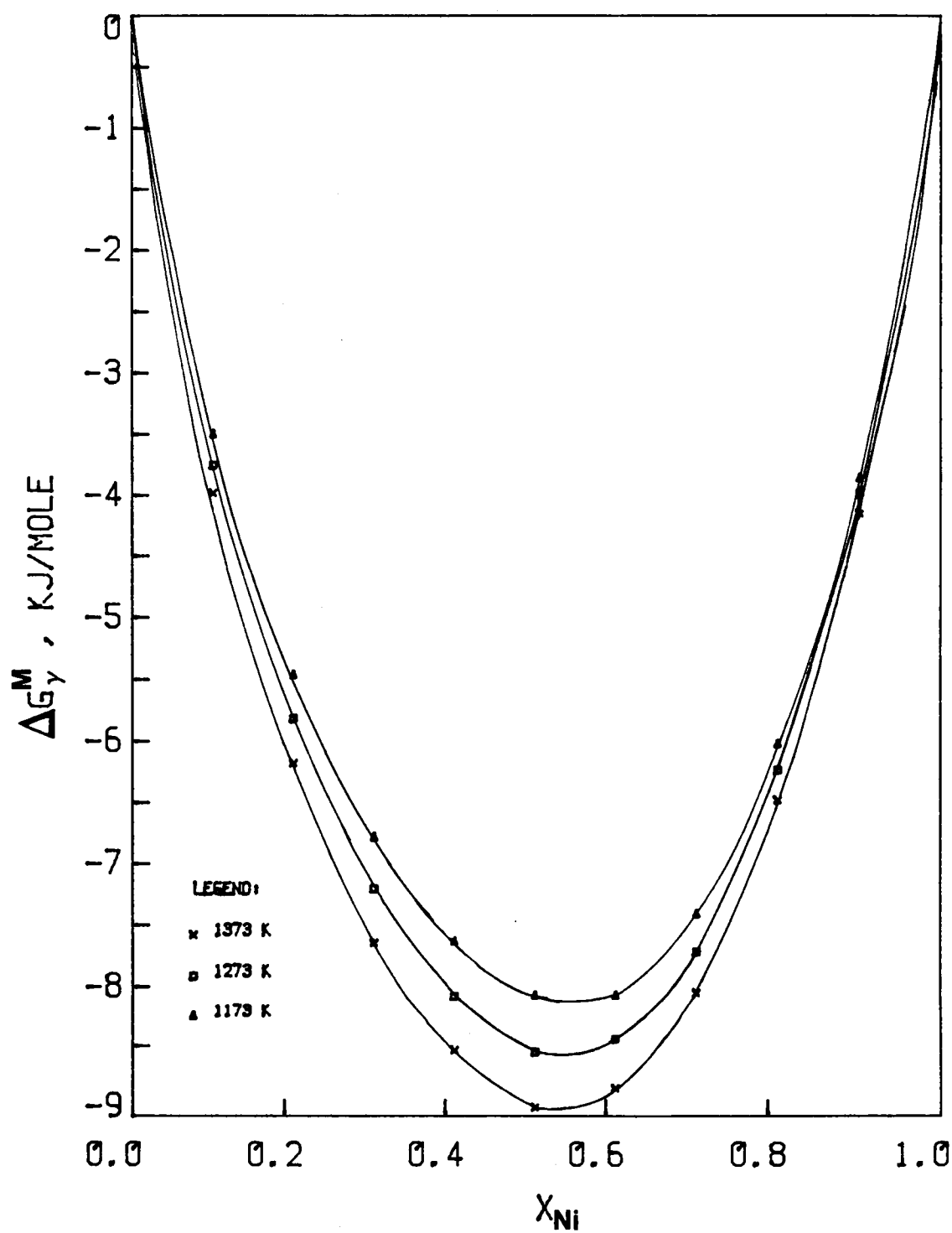


Figure II-6. Plot of ΔG_y^F vs. X_{Ni} at different temperatures (Henriet et al. (18)).

more convenient to choose the f.c.c. state as a standard for pure iron than the b.c.c. state because b.c.c. iron is ferromagnetic and the magnetic transition has a very strong effect on the thermodynamic properties. On the other hand, nickel is a more difficult case because f.c.c. nickel is ferromagnetic and there is no other stable solid phase. On the basis of this, f.c.c. state has been taken as the standard state. So, the modified Equation (5) for the free energy of formation of α phase with respect to pure f.c.c. Fe and Ni as the standard state is then:

$$\Delta G_{\alpha}^F = RT[X_{Ni} \ln X_{Ni} + (1 - X_{Ni}) \ln(1 - X_{Ni})] + X_{Ni} \Delta G_{Ni}^{\circ\gamma \rightarrow \alpha} + (1 - X_{Ni}) \Delta G_{Fe}^{\circ\gamma \rightarrow \alpha} \quad (6)$$

where $\Delta G_{Ni}^{\circ\gamma \rightarrow \alpha}$ and $\Delta G_{Fe}^{\circ\gamma \rightarrow \alpha}$ are the standard free energy of transformations of $\gamma \rightarrow \alpha$ in pure nickel and iron, respectively. Because f.c.c. nickel is the only stable phase, no reliable data are available on the standard free energy of transformation of $\gamma \rightarrow \alpha$ in pure nickel in the literature. Thus, the value of ΔG_{α}^F , and hence the calculated α - γ boundary, may be very sensitive to the data of $\Delta G_{Ni}^{\circ\gamma \rightarrow \alpha}$ used in our present calculations.

Study (14) on the heat capacity of disordered Ni_3Fe has enabled the accurate determination of the free energy of formation of Ni_3Fe in the temperature range 200-700°K. The heat of transformation is 3680 Joules/mole and the temperature of transformation at 773°K; thus, the free energy of formation of Ni_3Fe at any temperature can then be described by:

$$\Delta G_{\text{Ni}_3\text{Fe}}^{\text{F}} = RT[0.75 \ln 0.75 + 0.25 \ln 0.25] \\ + \Delta G_{\text{Ni}_3\text{Fe}}^{\text{XS}} + [-3680 + 4.76 T] . \quad (7)$$

The first term in Equation (7) describes the ideal term; the second term represents the nonideality, i.e., the excess properties which can be obtained by substituting $X_{\text{Ni}} = 0.75$ in Equation (1). The third term contributes to the free energy of transformation based on the data of Kollie et al. (14). Here, it is assumed that $\Delta C_p = 0$ so that the free energy of transformation is to be independent of temperature. This is justified as the contribution of ΔC_p to the free energy of formation at lower temperatures was found to be negligible. Taking C_p of Fe, Ni and Ni_3Fe from (30), (31), and (14), respectively, the contribution of ΔC_p to Equation (7) was found to be only 80 Joules/mole maximum in the temperature range of 900-500°K.

Thus, Equations (1) and (7) show that the free energy of formation of Ni_3Fe varies linearly with the temperature. The free energy of formation obtained by Equation (7) at various temperatures has been fitted to a linear equation using least square program.

B. COMPUTER PROGRAM

There exists a FORTRAN program TAN2.MIC in this Department which has been used to determine the α - γ phase boundary. TAN2.MIC program was adapted from Perkins et al. (63). The main program TAN2.MIC calls several function subprograms and subroutines. The sequence of the basic algorithm is as follows:

- (a) Determines the intersection points of the two free energy curves under consideration.

- (b) Determines which free energy curve is higher just to the left of intersection and then draws tangent to the lower curve.
- (c) Calculates the difference between the tangent to the lower curve and the higher free energy curve.
- (d) If crosses over, i.e. (the difference calculated as a function of composition is both positive and negative), the tangent steps back again.
- (e) Steps back until the tangent does not intersect the higher curve.
- (f) Bisects the last two values of X until the difference between the last two values of X becomes less than 10^{-6} and also the difference calculated in (c) at the average of the last two values calculated in (f) is positive. This gives the points of common tangency.

A flow chart for the different function subprograms and subroutines used is given in Figure II-7 and their functions are listed in Table II-1. The program was run on a DEC-10 system.

C. RESULTS

Thermodynamic properties of the Fe-Ni system used in our calculations are tabulated in Table II-2. The standard free energy of transformation of γ to α phase for iron and nickel has been taken from McElroy (32) and Kaufman et al. (25), respectively. Their values have been fitted to quadratic equations using a least square program. The computer program discussed previously and available in this Department

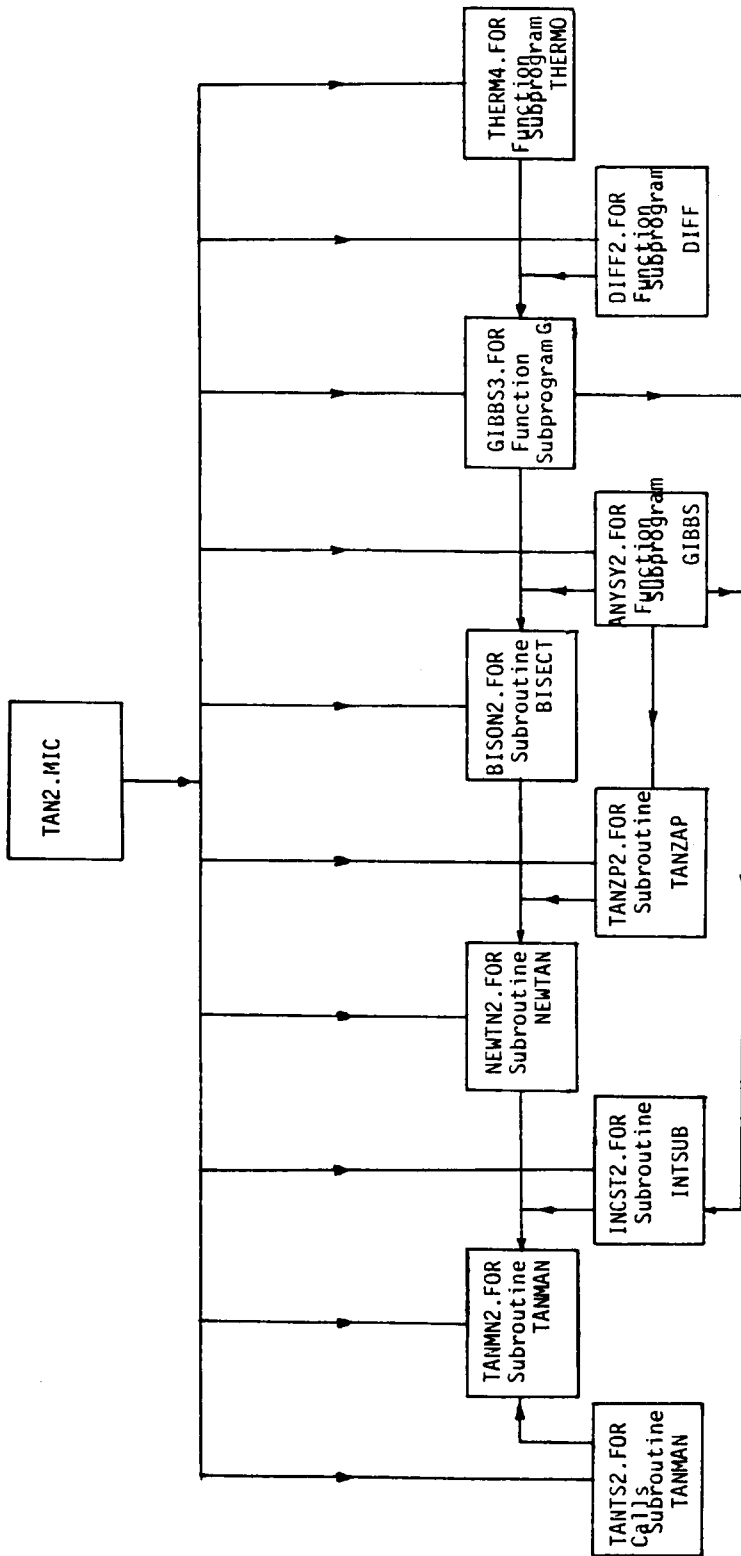


Figure II-7. A flow chart of the different function subprograms and subroutines used.

TABLE II-1
FUNCTION OF DIFFERENT SUBROUTINES AND FUNCTION
SUBPROGRAMS USED IN COMPUTER PROGRAM

Subroutine/ Function Subprogram	Function
TANMAN	Calls all subroutines and function subprograms and prints out the output.
INTSUB	Determines points of intersection.
NEWTAN	Serves as the main program for the common tangent subroutines and hence sets up boundary parameters.
TANZAP	"Zaps in" on the left point of common tangency.
BISECT	Finds the minimum of the right-hand side of the difference function.
G	Builds the total Gibbs free energy equation for any phase of any system and its first and second partial derivatives.
GIBBS	Nonideal portion of the Gibbs free energy equation and their first and second partial derivatives.
DIFF	Defines the difference function between a G function and the tangent to a G function.
THERMO	Builds various thermodynamic functions in X and T for binary systems.

TABLE II-2
THERMODYNAMIC PROPERTIES OF THE Fe-Ni SYSTEM

$$\Delta H_Y^M = X_{Ni}(1 - X_{Ni})[-11184.10 + 10282.62 (1 - 2X_{Ni}) - 5222.34 (1 - 2X_{Ni})^2] \text{J/mole}$$

$$\Delta S_Y^{XS} = X_{Ni}(1 - X_{Ni})[-6.37 + 3.65 (1 - 2X_{Ni})] \text{J/mole-K}$$

$$\Delta G_{Fe}^{\circ Y \rightarrow \alpha} = [-8271.81 + 11.65T - 0.0038T^2] \text{J/mole}$$

$$\Delta G_{Ni}^{\circ Y \rightarrow \alpha} = [2845.56 + 4.5455T - 0.00272T^2] \text{J/mole}$$

$$\Delta G_{Ni_3Fe}^F = [-6985.89 + 1.6238T] \text{J/mole}$$

has been used to determine the α - γ boundary, assuming α to behave as an ideal solution. The α - γ phase boundary was found to be very sensitive to the form of standard free energy of transformation equation of iron rather than of nickel. The temperature of transformation of iron was lowered by 40°K when the form of the standard free energy of transformation equation of iron was taken as linear function of temperature. Using Equations (4), (6), and (7) for γ , α , and Ni_3Fe , respectively, the γ - Ni_3Fe and α - Ni_3Fe boundaries have been determined graphically. The calculated phase boundaries are shown in Figure II-8 and also tabulated in Table II-3. The eutectoid transformation was found to be at 565°K, 52 at% Ni, and the maximum solubility of nickel in the b.c.c. phase is near 9%.

As shown in Figure II-8, the calculated α - γ phase boundary is in very good agreement with the recent experimental work of Romig et al. (13). The calculated eutectoid temperature at 565°K is in good agreement with the value of 618°K based on the work of Heumann et al. (33) as proposed by Shunk (2). The calculated solubility limit of nickel in the b.c.c. phase is near 9%, in contrast to near 4% as calculated by Kaufman et al. (11). But, this has also been observed to be near 6% (33,34). The γ - Ni_3Fe boundary is in good agreement with the proposed diagram of Shunk (2), considering that the present model of Ni_3Fe does not allow for loss of order with the increasing temperature. The ordering relationships of Ni_3Fe have been clarified by the use of Mössbauer spectroscopy in a recent paper (35). But due to its limitation to a very narrow temperature range, the results are not suitable for comparison with our present calculation.

TABLE II-3
CALCULATED PHASE BOUNDARIES OF THE Fe-Ni SYSTEM

Temperature °K	Solubility Limits	
	α Phase X_{Ni}	γ Phase X_{Ni}
<u>α-γ Phase Boundary</u>		
1100	0.004	0.010
1000	0.033	0.076
900	0.061	0.154
800	0.082	0.251
700	0.091	0.372
600	0.088	0.486
500	0.078	0.568
<u>γ-Ni₃Fe Phase Boundary</u>		
773	0.750	0.75
700	0.625	0.75
650	0.590	0.75
600	0.560	0.75
550	0.510	0.75
<u>α-Ni₃Fe Phase Boundary</u>		
500	0.075	0.75
400	0.035	0.75
300	0.025	0.75

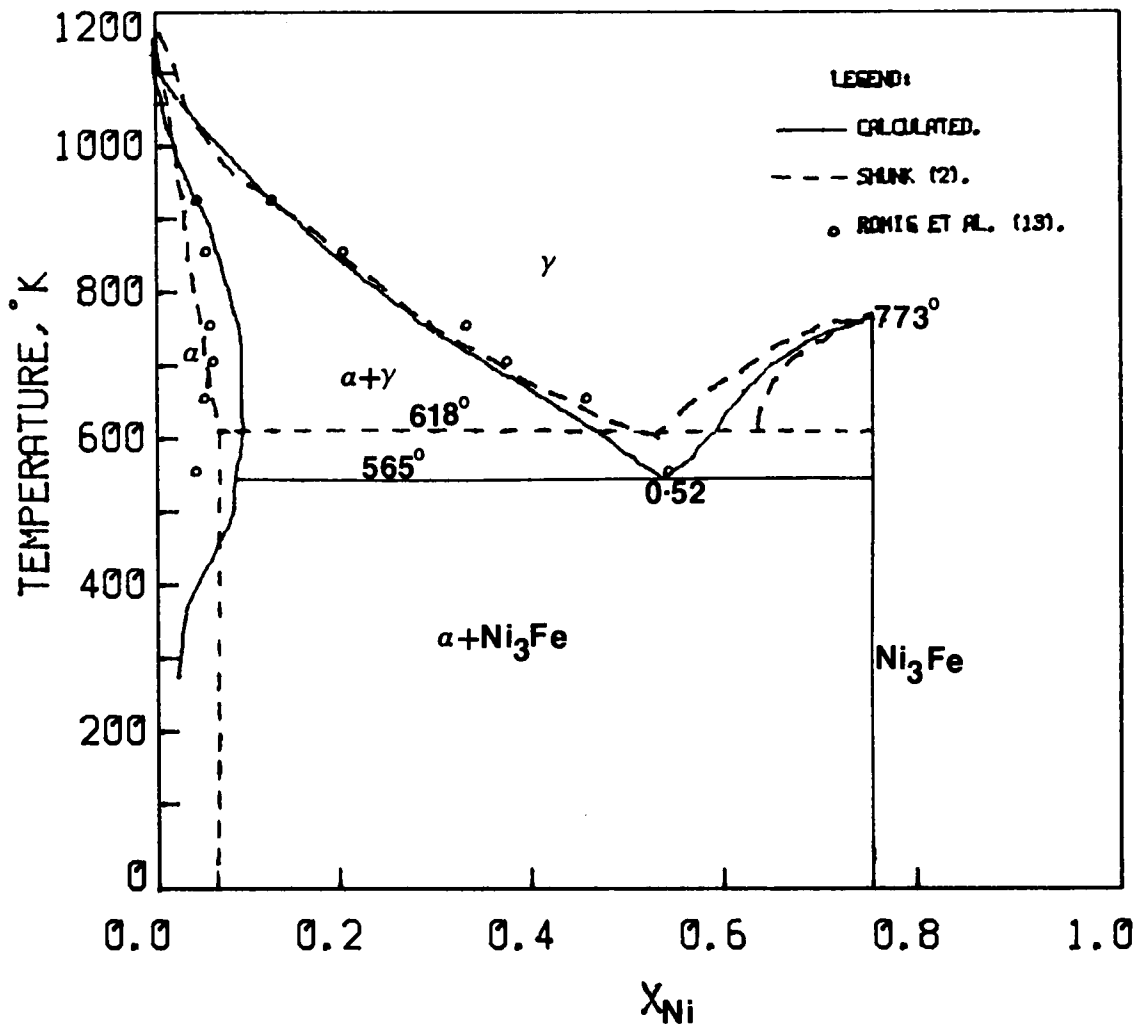


Figure II-8. Calculated Fe-Ni phase diagram.

CHAPTER IV

DISCUSSION

The calculated α - γ phase boundary is in very good agreement with the recent experimental work of Romig et al. (13) as shown in Figure II-8. The slight discrepancy in the calculated $\alpha/\alpha + \gamma$ boundary may be due to the simplified assumption of α being an ideal solution. But according to Kaufman et al. (25), the excess free energy of mixing for b.c.c. phase is positive; for example, at 800°K for $X_{Ni} = 0.5$ the value is 116.4 Joules/mole. This small nonideal positive value will not contribute much to the free energy of formation of α phase (ΔG_{α}^F : Equation (6), Chapter III) which, assuming ideal solution, at 800°K for $X_{Ni} = 0.5$ is about 2980 Joules/mole, and thus will not affect the calculated α - γ boundary. So the assumption of ideal behaviour of α alloys is quite justified. The positive value for the excess free energy of mixing for b.c.c. phase would shift the present boundaries to the left. The degree of accuracy of our present calculation of the α - γ boundary does not depend on the reliability of the data of standard free energy of transformation of $\gamma \rightarrow \alpha$ of nickel used here. It was found that the α - γ boundary was quite sensitive to the form of representation and the actual data of the standard free energy of transformation of $\gamma \rightarrow \alpha$ of iron rather than nickel. Recalling that the least negative data of ΔH_{γ}^M reported to this date of Henriot et al. (18) have been used in our present calculations, the excellent agreement of the calculated α - γ boundary with the experimental one proves the fact that the heat of mixing of γ alloys is indeed

more positive than the values reported by the other investigators (15-17,19-21). When ΔH_{γ}^M was more negative by 1000 Joules/mole than the data of Henriot et al. (18), α and γ boundaries shifted by 1% and 2%, respectively, towards lower values than the present calculated boundaries.

Due to the absence of any well-established model to take into account the effect of the loss of ordering with the increasing temperature on $\Delta G_{Ni_3Fe}^F$, proper calculation could not be made with the γ -Ni₃Fe boundary. Kaufman et al. (25) obtained the same eutectoid temperature of 618°K by calculation as that of proposed in the phase diagram of Shunk (2). But the accuracy of this eutectoid temperature of 618°K is questionable because they (25) chose the heat of order-disorder transformation to be 9609 Joules/g-atom, realizing that this value might be too high. Then, maybe 618°K, which was obtained by the conventional equilibration technique (33), is not the equilibrium eutectoid temperature. Lack of thermodynamic data on ordered NiFe has made us exclude NiFe from consideration in our present calculations. The tendency to immiscibility in the Fe-Ni (f.c.c.) system as was reported by Tanji et al. (17) was not found here. It may be that the energy difference between the ΔG versus concentration curve and its common tangent is too small to allow the nucleation of the two phase separation.

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