THERMODYNAMIC PROPERTIES OF SOLID ALLOYS
OF CHROMIUM WITH NICKEL AND IRON

Final Report

F. N. Mazandarany and R. D. Pehlke

The University of Michigan
Ann Arbor, Michigan

April 1, 1968 - June 30, 1972

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UNDER CONTRACT NO. AT(11-1)-1791

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Thermodynamic Properties of Solid Alloys:
of Chromium with Nickel and Iron

by

F. N. Mazandarany and R. D. Pehlke*

ABSTRACT

The thermodynamic properties of chromium have been determined in the Ni-Cr and Fe-Cr binary systems and in the Fe-corner of the Fe-Ni-Cr system. These properties are based on experimental measurements using solid oxide electrolyte cells of the type: $\text{Cr}, \text{Cr}_2\text{O}_3 | \text{ThO}_2 - \text{Y}_2\text{O}_3 | \text{Cr (alloy)}, \text{Cr}_2\text{O}_3$.

In the Ni-Cr system, between 900 and 1300°C, the activity of chromium exhibits negative deviation from ideality up to about 25 a/o chromium. For alloys higher in chromium content, the activity of chromium exhibits positive deviation from ideality. In the Fe-Cr system, between 900 and 1200°C, and zero and 63 a/o Cr, the chromium activity when referred to solid pure chromium exhibits positive deviation from ideality in both the γ and α phases, approaching ideality with increasing temperature. The nickel and iron activities in these two respective binary systems were calculated by a Gibbs-Duhem integration.

The activity of chromium, referred to solid pure chromium, was measured between 900 and 1200°C in solid Fe-Ni-Cr alloys with chromium concentrations of 9, 20, and 30 a/o and Ni concentrations of 8, 18, and 30 a/o. Additions of nickel to Fe-Cr alloys in the above concentration range are found to increase the chromium activity. The effect of nickel in increasing the chromium activity is greater at both greater chromium contents and lower temperatures.

F. N. Mazandarany, formerly Graduate Student at The University of Michigan, is Staff Associate, Gulf Energy and Environmental Systems, LaJolla, California. R. D. Pehlke is Professor of Metallurgical Engineering, The University of Michigan, Ann Arbor, Michigan. This paper is based on a portion of a thesis submitted by F. N. Mazandarany in partial fulfillment of the requirements for the degree Doctor of Philosophy at The University of Michigan.

ACKNOWLEDGEMENT

This work was supported in part by the United States Atomic Energy Commission under contract No. AT(11-1).

INTRODUCTION

The thermodynamic properties of chromium in solid alloys with iron and nickel have been previously investigated by various techniques⁽¹⁻¹¹⁾. There is, in general, substantial disagreement among the results obtained by various investigators using different or even similar techniques. The various techniques employed previously include gas equilibration, vapor pressure and electrochemical techniques.

The purpose of the present investigation was to measure the thermodynamic activity of chromium in solid Fe-Cr binary, Ni-Cr binary and Fe-rich-Ni-Cr ternary alloys employing the solid oxide electrolyte (S.O.E.) technique with yttria-doped-thoria (YDT) as the solid electrolyte. Reversible potential measurements on cells of the type $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2 - 8 \text{ m/o YO}_{1.5} | \text{Cr(alloy), Cr}_2\text{O}_3$ were used to determine the Cr activity in the solid alloys.

In an oxygen concentration cell of the type employed, the electrode reactions may be written as:

The net cell reaction is:

Under isothermal, isobaric and reversible conditions, the Gibbs free energy change for the reaction of Equation 3 is given by:

$$\Delta \bar{G}_{\text{Cr}} = \bar{G}_{\text{Cr}} - \bar{G}_{\text{Cr}}^{\circ} = - 3EF = RT \ln a_{\text{Cr}} \quad (4)$$

or
$$a_{\text{Cr}} = \exp\left(-\frac{3EF}{RT}\right) \quad (4a)$$

where a_{Cr} is the chemical activity of Cr in the alloy, referred to a standard state of oxygen-saturated pure Cr of unit activity, E is the

open-circuit cell potential in volts, F is Faraday's constant (23066 cal per volt-gram equivalent), R is the universal gas constant (1.987 cal per gram equivalent-°K) and T is the cell temperature in °K.

The requirement of reversible (open-circuit) potential measurements demands that the individual electrode reacting be singularly defined by Equations 1 and 2 and that no currents be present in the cells as a result of a partial electronic conduction in the electrolyte or other sources (such as electromagnetic fields).

The available literature on the Cr-O system⁽¹²⁾ indicates that Cr_2O_3 is the only oxide in equilibrium with metallic Cr from 780-1300°C. There is no measurable solid solubility (non-stoichiometry) in the Cr, Cr_2O_3 system. The possibility of a number of exchange reactions involving spinel formations within the alloy electrodes was thermodynamically considered. Available free energy data^(13,14) were used to show that the oxide phase in equilibrium with Fe-Cr, Ni-Cr and Fe-Ni-Cr alloys where the Cr activity does not fall below $\sim 10^{-4}$ would consist entirely of Cr_2O_3 (NiCr_2O_4 and FeCr_2O_4 are unstable above this Cr activity). In view of the relatively high Cr contents (>3%) used in the alloys such side reactions were not expected. A direct experimental verification of this conclusion is reported below.

Yttria-doped-thoria electrolytes have been the subject of numerous conductivity⁽¹⁵⁻¹⁹⁾ and thermodynamic⁽¹⁷⁻²⁰⁾ investigations. It is invariably believed that adequately prepared electrolytes of thoria show ion conduction down to a range of oxygen potentials well below that of the Cr, Cr_2O_3 equilibrium, e.g. those associated with the Mn, MnO equilibrium. The reversibility of cells involving Cr, Cr_2O_3 electrodes and thoria-yttria electrolytes were demonstrated by the authors in an experimental study of the Cr, Cr_2O_3 system⁽²¹⁾.

EXPERIMENTAL TECHNIQUE

Equipment

The galvanic cell arrangement used in this study is schematically shown in Figure 1. The details of the cell, its construction and assembly, as well as the experimental procedures are given elsewhere⁽²¹⁾. Briefly, the cell consists of a ThO_2 -8 m/o $\text{YO}_{1.5}$ electrolyte pellet sandwiched between two electrodes. Cell potentials were measured with a high impedance (10^7 ohms) potentiometric voltmeter (Keithly Model 660). Temperature was measured with a Pt/Pt-10Rh thermocouple and a Model K-2 L & N potentiometer. The atmosphere in the cell was purified argon, maintained at a positive pressure of ~2 cm Hg.

Materials

ThO_2 -8 m/o $\text{YO}_{1.5}$ electrolyte pellets were obtained from the Zirconium Corporation of America*. The $\text{Cr, Cr}_2\text{O}_3$ electrodes were prepared by mixing high purity Cr powder (99.5%)[†] with analytical grade Cr_2O_3 powder in a 10/1 wt ratio, and compressing in a steel die at about 60 KSI to obtain pellets with the dimensions; 6 mm diameter by 2 mm high. The pressed pellets were sintered in dry argon for 24 hours at 1000°C. The sintered pellets were polished on a 50- μ polishing wheel before use in a cell.

The preparation of the alloy electrodes consisted of two steps. First, the high purity elements were melted to produce the desired alloys. Secondly, sufficient amounts of the alloys were either filed or machined to produce relatively fine particles for subsequent pelletizing.

In melting the high purity elements (99.5+ % electrolytic grade Cr, 99.95+ % Ferrovac E grade Fe and 99.8+ % SF grade Ni), sufficient amounts of the element were weighed and placed in a high purity alumina crucible.

*for details, see reference 21

†major impurities were Fe(.13%), Si(.02%), Al(.03%), S(.027%), N(.041%), and O(essentially the remainder).

The 100-150 gm charge was melted inductively under dry argon. After sufficient time had been allowed for complete melting and homogenization, approximately 25 gms of the melt were sucked into a 5 mm I.D. vycor tube through a sealed opening in the melting chamber and immediately quenched in water. Sufficient amounts of the elements, precalculated and preweighed, were added to the remaining melt from the same opening to change the alloy composition. This procedure was repeated 3 to 5 times. During the period when the chamber was open for addition of alloying elements or insertion of the sampling tube, very high flows of argon were used to minimize contamination of the melt by nitrogen in the air. This procedure produced alloy rods of 4 mm diameter and 250 mm length. About 35 mm was discarded from each end. Other cuts at 40-50 mm lengths showed no evidence of porosity. There was a very thin scale of Cr_2O_3 on the surfaces of the rods which was removed by grinding.

All of the Fe-Cr and Fe-Ni-Cr alloys studied were soft enough to be easily filed. Filings of these alloys were prepared by holding a steel file against each alloy rod as the rod was rotated in a drill press at low speeds. The filings were collected on a piece of paper underneath the rod. It was observed that the file "teeth" withstood this operation without evidence of substantial wear. Ni-Cr alloys with 40% Cr or less were also filed in the same manner as above. Ni-Cr alloys with nominally 60 and 67 wt pct Cr were too hard to file and too tough to pulverize. These two alloys were machined to produce shavings for pelletizing. Between 5 and 10 gms of either filings or shavings were prepared from each alloy. A few gms of alloy filings or shavings of each composition were mixed with about one half the volume of Cr_2O_3 . Pellets of the same size as the standard Cr, Cr_2O_3 electrodes (6 mm diameter and 2 mm high) were prepared by pressing at about 100 KSI. There was no need for sintering these pellets as they exhibited sufficient strength as pressed.

Small portions of the filings or shavings were used for chemical analysis. The Cr content was determined by a persulfate oxidation method in the Department of Materials and Metallurgical Engineering, The University of Michigan. The expected accuracy of better than 1 percent of the chromium present was demonstrated by analysis on precisely weighed and mixed pure Cr, Fe and Ni as well as on precisely weighed amounts of anhydrous potassium dichromate. Nickel and iron contents of binary alloys were determined by difference from 100 percent. The nickel content of the ternary alloys was determined by the standard dimethylglyoxime method in an outside laboratory. The expected accuracy for this analysis is better than 1 percent of the nickel present. Iron in ternary alloys was evaluated by difference from 100 percent. The summary of chemical analysis of the alloys studied is presented in Table I.

Kjeldahl analyses for nitrogen were performed on some of the alloys in the Department of Materials and Metallurgical Engineering, The University of Michigan. Nitrogen levels were found to be about 500 ppm in high chromium alloys and below 100 ppm in low chromium alloys. These levels of nitrogen could be expected from the nitrogen impurity level in the elemental chromium used in the preparation of alloys (~500 ppm).

Procedure

The experimental procedure has been described in detail previously⁽²¹⁾. Briefly, the assembled cell was placed vertically in the hot zone of a Marshall Pt-resistance furnace. The cell was evacuated several times and filled with purified argon at room temperature. After the final evacuation and filling, the furnace was turned on to heat the cell to an intermediate temperature ($\approx 1000^{\circ}\text{C}$). After thermal equilibrium ($\pm 0.5^{\circ}\text{C}$) was attained, the cell was allowed to come to thermodynamic equilibrium over the next 5 to 12 hours. Criteria for attainment of

thermodynamic equilibrium were adopted such that at constant temperature the measured cell potential should not vary by more than ± 0.5 mv over a period of one hour and that such variations be random and not systematic. Equilibrium potential measurements were made at approximately 25°C intervals over the temperature range of interest on both heating and cooling over a period of 3 to 6 days.

Reversibility in the cells was generally inferred from the high stability of measured potentials and high linearity of cell potential-temperature relationships, which were unaffected by temperature cycling and reproducible from run to run. Additional evidence for the reversible behavior of the cells is discussed later.

RESULTS AND DISCUSSION

Ni-Cr System

The experimental data are plotted in Figure 2. The dashed line indicates that due to the very slow rate of approach to equilibrium in the cell no measurements were made in that temperature range. Table II summarizes the experimental data on solid Ni-Cr binary alloys. The emf-temperature relationships given in Table II were determined by least-squares analyses of the experimental data. The data for the three two-phase alloys with 49, 63, and 70 a/o chromium were treated as one set of data in the least square analysis because there was no evidence of any systematic difference in the nature of the scatter between three independent runs made on these three alloys. The temperature range from 1180-1300°C in these two-phase alloys was carefully investigated to see if there was any indication of the eutectoid transformation at 1218°C suggested by Grant, et al. (22,23). There was no evidence of such a transformation as

shown by the lack of any discontinuity in the emf-temperature line beyond the limits of the usual scatter in the data.

Two independent runs were made on the 21 a/o chromium alloy to check the reproducibility of the experimental data between "duplicate" runs. Table III summarizes these results comparing the chromium activities and activity coefficients determined in the two runs. Table IV summarizes the experimentally determined properties of chromium in solid Ni-Cr alloys. Figure 3 is a plot of the chromium activity in the binary system. The phase boundaries proposed by Hansen⁽¹²⁾ are superimposed on this plot. The experimentally determined chromium activities are consistent with the phase diagram proposed by Hansen.

In an effort to compare the activity of chromium in solid Ni-Cr alloys reported by previous investigations with the results of this study, the activity plots of Figure 3 for 1000 and 1300°C are replotted in Figure 4, showing the results of other investigators as well. There appears to be reasonable agreement among various investigators below 25 a/o chromium, indicating a slight negative deviation from ideality. The relatively large negative deviations reported by Grube and Flad⁽¹⁾ near the miscibility gap are unusual. Reported activities by Pugliese and Fitterer⁽⁴⁾ were not included in Figure 4 because of internal inconsistencies in their measurements. These investigators measured emf's of cells, Cr (in Ni), $\text{Cr}_2\text{O}_3|\text{ZrO}_2\text{-CaO}|\text{air}$, and compared these emf's with those from the cell, $\text{Cr, Cr}_2\text{O}_3|\text{ZrO}_2\text{-CaO}|\text{air}$, to determine the chromium activity. However, differences between emf's of these two cells were either too low or even negative, corresponding to chromium activities too high or even greater than unity. In an attempt to resolve these anomalies, Pugliese and Fitterer averaged the emf's of the latter cell, $\text{Cr, Cr}_2\text{O}_3$ versus air, with those of Tretjakow and Schmalzried⁽¹³⁾ for the same

cell. This procedure introduced large uncertainties in the reported chromium activities, as well as resulting in a positive temperature dependence of chromium activity in the α and $\gamma + \alpha$ regions (negative $\Delta \bar{H}_{Cr}$), which is inconsistent with the calorimetric measurements of Dench⁽²⁴⁾.

Figure 5 is a plot of the calculated Ni activities. The Ni activities were calculated by graphical integrations of the Gibbs-Duhem equation using Darken's⁽²⁵⁾ method; where:

$$RT \ln \gamma_{Ni} = -X_{Ni} X_{Cr} \alpha_{Cr} + \int_0^{X_{Cr}} \alpha_{Cr} dX_{Cr}; \quad (5)$$

γ_{Ni} is the activity coefficient of Ni $\equiv a_{Ni}/X_{Ni}$ and

$$\alpha_{Cr} \equiv \frac{RT \ln \gamma_{Cr}}{(1-X_{Cr})^2}. \quad (6)$$

The chromium and nickel Henrian activity coefficients (γ_{Cr}° and γ_{Ni}°) are related to α_{Cr} by the following expressions, respectively⁽²⁶⁾.

$$\ln \gamma_{Cr}^\circ = \frac{(\alpha_{Cr})_{X_{Cr}=0}}{RT} \quad (7)$$

$$\ln \gamma_{Ni}^\circ = \frac{\int_0^1 \alpha_{Cr} dX_{Cr}}{RT} \quad (8)$$

Table V summarizes γ_{Cr}° and γ_{Ni}° calculated from Equations 7 and 8, respectively.

Fe-Cr System

The experimental data, summarized in Table VI, are presented graphically in Figure 6. In the case of the alloy with 3.9 a/o chromium, one of the electrode lead wires broke and the run had to be terminated before any

data were taken below 950°C. The rate of equilibration in the alloy with 63.1 a/o chromium below 975°C was too slow to make meaningful measurements below this temperature.

Reproducibility was demonstrated in this system by duplicate measurements on two cells using a 19 a/o chromium alloy. The chromium activities and activity coefficients determined in these experiments are compared in Table VII.

Plots of the chromium activity in the binary system are shown in Figure 7. The activity plots have been drawn consistent with α and γ phase boundaries given by Hansen⁽¹²⁾. Table VIII summarizes the experimentally determined thermodynamic properties of chromium in binary Fe-Cr alloys.

In an attempt to compare the results of previous investigators with those of this study, the chromium activity at 1200°C has been replotted in Figure 8, showing the results of other investigators. The range of activities reported includes negative deviation, nearly ideal and highly positive deviations. There appears to be reasonable agreement among the various investigators at low chromium levels, the degree of agreement becoming poorer with increasing chromium content.

The activity of Fe was calculated by the Gibbs-Duhem equation in a similar fashion as in the Ni-Cr system. Figure 9 is a plot of the calculated Fe activities. The calculated Henrian activity coefficients in the Fe-Cr system are given in Table IX.

Fe-Ni-Cr System

Plots of the experimental data for each alloy are shown in Figure 10. Table X summarizes the experimental data. Table XI summarizes the experimentally determined thermodynamic properties of chromium in the

ternary alloys. Figure 11 shows the effect of increasing nickel content on the activity of chromium. The constant chromium levels shown in Figure 11 are the average of three alloys with slightly different chromium contents. The activity curves in Figure 11 were drawn in accordance with isothermal ternary sections given by Jenkins, et al.⁽²⁷⁾.

The activities of chromium in the 9 a/c chromium isocomposition alloys (bottom two lines in Fig. 11) extrapolate to the corresponding activities in the Fe-Cr binary alloy (obtained from Figure 7). This is in support of the overall consistency and accuracy of the experimental data.

Figure 11 indicates that the effect of nickel in increasing the chromium activity is greater at both higher chromium contents and lower temperatures. This behavior is consistent with the thermodynamic properties of the Fe-Cr and Fe-Ni binary systems. Ni shows large negative deviation when added to Fe⁽²⁸⁾. The experimental results of this study indicate that Ni deviates positively when added to Cr. Thus, the expected effect of adding Ni to Fe-Cr alloys is to increase the Cr activity. This finding is also in general agreement with the Cr activity measurements of Slough, et al.⁽¹¹⁾ in Fe-Cr-Ni alloys, using the Knudsen effusion technique.

Experimental Verification of the Reversibility of Electrodes

As discussed previously, an indication of the high degree of reversibility in the measured potentials was provided by highly stable emf's unaffected by temperature cycling, a high degree of reproducibility for duplicate runs and a high linearity of the emf-temperature lines with standard deviations usually on the order of 0.6 mv. Additional experimental verifications on the reversibility of the $\text{Cr, Cr}_2\text{O}_3$ electrode are given elsewhere⁽²¹⁾.

The reversibility of alloy electrodes was further verified by comparing the measured emf of the cell $\text{Fe-18 Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Fe-30 Cr, Cr}_2\text{O}_3$ with that calculated by the difference of the measured emf's of the two cells, $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Fe-18 Cr, Cr}_2\text{O}_3$ and $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Fe-30 Cr, Cr}_2\text{O}_3$. Table XII shows the results. The agreement between the calculated and measured emf's (cells 3 and 4 in Table XII) is within the expected experimental error band ($v .6 \text{ mv per cell} = \pm 1.8 \text{ mv}$).

Another experimental verification of the alloy electrode reversibility was made by an electron microprobe analysis of two alloy electrodes after they had been used in a cell. Figure 12 shows photographs of (a) Cr K_α and (b) Fe K_α radiations from the (Fe-8 Cr, Cr_2O_3) electrode. Comparison of photographs (a) and (b) shows that the Cr_2O_3 particle is essentially free of Fe. There is no indication of transfer of Fe from the alloy matrix to the Cr_2O_3 particle.

Figure 13 shows photographs of (a) Cr, (b) Fe and (c) Ni K_α radiations from the (Fe-8Cr-8Ni, Cr_2O_3) electrode. Again, comparison of photographs (a), (b), and (c) shows no evidence of either Fe or Ni transport from the alloy matrix to the Cr_2O_3 particle. The Cr_2O_3 particle appears to be substantially free of both Ni and Fe. The slight amount of Ni K_α radiation apparent in the oxide is mainly background radiation.

CONCLUSIONS

In the Ni-Cr system, from 1000-1300°C, the chromium activity deviates negatively from Raoultian behavior up to 20-25 a/o chromium and positively above these concentrations up to the highest concentration studied, 70 a/o chromium. The chromium activity coefficient decreases with increasing temperature in the direction of ideality. The results are in agreement with the phase diagram proposed by Hansen and indicate no evidence of a eutectoid reaction in the system.

In the Fe-Cr system, from 900-1200°C, the chromium activity deviates positively in both the γ and α phases for alloys studied up to 63 a/o chromium. The chromium activity coefficient in all alloys decreases in the direction of ideality with increasing temperature.

At substantially constant chromium contents of nominally 9, 20, and 31 a/o chromium in Fe, additions of 8, 18, and 30 a/o Ni increase the Cr activity in the Fe-Cr-Ni system in the temperature range from 900-1200°C. The effect of temperature is similar to that in the binary systems; the chromium activity coefficient decreases with increasing temperature. The effect of nickel in increasing the chromium activity is stronger at higher chromium contents and lower temperatures.

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TABLE I

Chemical Analysis of Alloys Studied

Alloy Designation	Cr Content		Ni Content		Fe Content
	w/o	a/o	w/o	a/o	
<u>Ni-Cr Alloys:</u>					
Ni-10Cr	10.14	11.50	balance		- - - -
Ni-15Cr	14.17	15.95	balance		- - - -
Ni-20Cr	19.05	21.00	balance		- - - -
Ni-25Cr	24.29	26.50	balance		- - - -
Ni-35Cr	37.13	39.00	balance		- - - -
Ni-45Cr	46.01	49.00	balance		- - - -
Ni-60Cr	60.02	63.00	balance		- - - -
Ni-67Cr	67.33	70.00	balance		- - - -
<u>Fe-Cr Alloys:</u>					
Fe-4Cr	3.62	3.90	- - - -		balance
Fe-8Cr	6.49	6.80	- - - -		balance
Fe-18Cr	17.93	19.0	- - - -		balance
Fe-30Cr	30.21	31.7	- - - -		balance
Fe-45Cr	46.03	47.8	- - - -		balance
Fe-60Cr	61.43	63.1	- - - -		balance
<u>Fe-Cr-Ni Alloys:</u>					
Fe-8Cr-8Ni	8.10	8.70	7.72	7.70	balance
Fe-8Cr-18Ni	8.42	9.00	16.97	15.40	balance
Fe-8Cr-30Ni	8.83	9.50	29.99	28.70	balance
Fe-18Cr-8Ni	19.20	20.40	7.85	7.20	balance
Fe-18Cr-18Ni	18.90	20.20	18.35	17.30	balance
Fe-18Cr-30Ni	18.5	19.90	30.33	28.80	balance
Fe-30Cr-18Ni	30.20	31.90	17.91	17.20	balance
Fe-30Cr-30Ni	31.70	33.80	29.49	27.75	balance

TABLE II

Experimental Data for Solid Ni-Cr Alloys*

x_{Cr}	$E(mv) \pm \sigma^{\dagger}$	$\Delta\bar{G}_{Cr}(cal)^{\#}$	Temperature range of measured E
0.115	$-20.48 + 0.0873T$ ± 0.6	$1420 - 6.04T$	1223 - 1553
0.160	$-19.33 + 0.0729T$ ± 0.4	$1340 - 5.04T$	1300 - 1560
0.210	$-31.75 + 0.0695T$ ± 0.6	$2200 - 4.81T$	1240 - 1560
0.265	$-49.81 + 0.0695T$ ± 0.2	$3450 - 4.81T$	1230 - 1570
0.390	$-48.30 + 0.0466T$ ± 0.6	$3340 - 3.22T$	1260 - 1530
0.490, 0.630 & 0.700	$-26.04 + 0.215T$ ± 0.8	$1800 - 1.49T$	1300 - 1570

* All temperatures in °K

† Line calculated by method of least squares; σ = standard deviation# Calculated from $\Delta\bar{G}_{Cr} = -3EF$

TABLE III

Comparison of Results from Two Independent Runs for Alloy Ni-21 Cr

T(°C)	E(mv)		a_{Cr}		γ_{Cr}	
	Run 51	Run 87	Run 51	Run 87	Run 51	Run 87
1000	57.09	56.12	0.210	0.215	0.999	1.026
1100	63.87	63.40	0.198	0.200	0.942	0.954
1200	70.64	70.67	0.188	0.188	0.896	0.896
1300	77.42	77.95	0.180	0.178	0.858	0.848

TABLE IV

Thermodynamic Properties of Cr in Solid Ni-Cr Alloys
Determined Directly From Cell Potentials*

X_{Cr}	T(°C)	E(mv)	$a_{Cr}^{\dagger}$	$-\Delta\bar{G}_{Cr}^{\ddagger}$	$\Delta\bar{H}_{Cr} = \Delta\bar{H}_{Cr}^{xs\ddagger}$	$\Delta\bar{S}_{Cr}^{\#}$
.115	1000	90.74	0.084	6280	1420	6.04
	1100	99.47	0.080	6880		
	1200	108.21	0.077	7490		
	1300	116.95	0.075	8090		
.160	1000	73.52	0.134	5090	1340	5.04
	1100	80.81	0.129	5590		
	1200	88.10	0.125	6100		
	1300	95.40	0.121	6600		
.210	1000	56.76	0.212	3930	2200	4.81
	1100	63.72	0.199	4410		
	1200	70.76	0.188	4890		
	1300	77.62	0.179	5370		
.265	1000	38.75	0.346	2680	3450	4.81
	1100	45.71	0.314	3160		
	1200	52.67	0.288	3640		
	1300	59.63	0.267	4130		
.390	1000	11.10	0.738	768	3340	3.22
	1100	15.76	0.670	1090		
	1200	20.43	0.617	1415		
	1300	25.10	0.574	1740		
.490	1000	1.30	0.965	90	1800	1.49
.631	1100	3.44	0.916	238		
&	1200	5.59	0.876	387		
.700	1300	7.74	0.843	535		

* All properties are referred to a standard state of oxygen-saturated solid pure Cr

$\dagger \pm 2\%$ based on standard error of estimate of emf.

$\ddagger$ In cal/g-mole

$\#$ In cal/deg/g-mole

TABLE V

Henrian Activity Coefficients in the Ni-Cr System

T(°C)	$\gamma_{\text{Cr}}^{\circ *}$	$\gamma_{\text{Ni}}^{\circ \dagger}$
1000	0.47	4.46
1100	0.47	3.66
1200	0.47	2.59
1300	0.47	2.08

* ± 0.02 † ± 0.10

TABLE VI

Experimental Data for Solid Fe-Cr Alloys*

X_{Cr}	$E(mv) \pm \sigma^\dagger$	$\Delta\bar{G}_{Cr}(cal)^\#$	Temperature range of measured E
0.039	$-65.48 + 0.1147T$ ± 1	$4530 - 7.94T$	1180 - 1480
0.069	$-58.17 + 0.0998T$ ± 0.6	$4020 - 6.91T$	1190 - 1480
0.190	$-60.36 + 0.0793T$ ± 0.3	$4180 - 5.49T$	1180 - 1490
0.317	$-41.67 + 0.0523T$ ± 0.4	$2880 - 3.62T$	1175 - 1480
0.478	$-26.34 + 0.0328T$ ± 0.4	$1820 - 2.27T$	1190 - 1490
0.631	$-21.61 + 0.0239T$ ± 0.3	$1490 - 1.65T$	1240 - 1485

* All temperatures in °K

† Line calculated by method of least squares; σ = standard deviation# Calculated from $\Delta\bar{G}_{Cr} = -3EF$

TABLE VII

Comparison of Results from Two Independent
Runs for Alloy Fe - 19Cr

T(°C)	E(mv)		a_{Cr}		γ_{Cr}	
	Run 86	Run 69	Run 86	Run 69	Run 86	Run 69
900	32.18	32.91	0.385	0.376	2.024	1.981
1000	40.20	40.83	0.333	0.327	1.752	1.722
1100	48.22	48.75	0.294	0.290	1.549	1.528
1200	56.25	56.68	0.264	0.262	1.392	1.378

TABLE VIII

Thermodynamic Properties of Cr in Solid Fe-Cr Alloys Determined
Directly From Cell Potentials*

x_{Cr}	T(°C)	E(mv)	$a_{Cr}^{\dagger}$	γ_{Cr}	$-\Delta\bar{G}_{Cr}^{\ddagger}$	$\Delta\bar{G}_{Cr}^{xs\ddagger}$	$\Delta\bar{H}_{Cr}^{xs\ddagger}$	$-\Delta\bar{S}_{Cr}^{xs\#}$	$\Delta\bar{S}_{Cr}^{\#}$
0.039	900	96.16	0.128	3.290	4790	2780	4530	2.37	7.937
	1000	80.64	0.110	2.824	5580	2620		2.06	
	1100	92.11	0.097	2.479	6370	2480		1.80	
	1200	103.59	0.086	2.214	7170	2330		1.58	
0.069	900	58.86	0.174	2.525	4070	2150	4030	1.84	6.906
	1000	68.84	0.152	2.205	4760	2000		1.57	
	1100	78.81	0.135	1.963	5450	1840		1.34	
	1200	88.79	0.123	1.776	6140	1680		1.14	
0.190	900	32.66	0.379	1.996	2260	1610	4180	1.37	5.487
	1000	40.59	0.329	1.734	2810	1390		1.09	
	1100	48.52	0.292	1.537	3360	1170		0.85	
	1200	56.45	0.263	1.386	3910	955		0.65	
0.317	900	19.66	0.558	1.760	1360	1327	2880	1.12	3.619
	1000	24.89	0.506	1.597	1720	1250		0.93	
	1100	30.12	0.466	1.469	2080	1050		0.76	
	1200	35.35	0.434	1.368	2440	916		0.62	
0.478	900	12.05	0.699	1.463	834	887	1820	0.76	2.581
	1000	15.32	0.658	1.376	1060	807		0.63	
	1100	18.60	0.624	1.305	1290	727		0.53	
	1200	21.87	0.596	1.247	1510	647		0.44	
0.631	900	6.46	0.825	1.308	447	626	1450	0.53	1.654
	1000	8.85	0.785	1.244	612	522		0.43	
	1100	11.24	0.752	1.192	778	478		0.35	
	1200	13.64	0.724	1.148	944	404		0.27	

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

$\dagger \pm 2\%$ based on standard error of estimate of emf

$\ddagger$ In cal/g-mole

$\#$ In cal/deg/g-mole

TABLE IX

Henrian Activity Coefficients in the Fe-Cr System

T(°C)	$\gamma_{\text{Cr}}^{\circ *}$	$\gamma_{\text{Fe}}^{\circ \dagger}$
900	4.89	4.25
1000	3.99	3.46
1100	3.35	2.89
1200	2.90	2.47

* ± 0.02 $\dagger \pm 0.05$

TABLE X

Experimental Data for Solid Fe-Ni-Cr Alloys*

x_{Cr}	x_{Ni}	$E(mv) \pm \sigma^\dagger$	$\Delta\bar{G}_{Cr}(cal)^\ddagger$	Temp. range of Measured E
0.087	0.070	$-65.89 + 0.1021T$ ± 0.3	4560 - 7.06T	1190 - 1490
0.090	0.154	$-71.67 + 0.1038T$ ± 0.3	4960 - 7.18T	1190 - 1480
0.095	0.287	$-65.03 + 0.0966T$ ± 0.5	4500 - 6.68T	1180 - 1495
0.204	0.072	$-66.44 + 0.0766T$ ± 0.1	4600 - 5.30T	1170 - 1480
0.202	0.173	$-67.46 + 0.0756T$ ± 0.4	4670 - 5.52T	1170 - 1480
0.199	0.288	$-75.11 + 0.0798T$ ± 0.3	5200 - 5.52T	1180 - 1495
0.319	0.172	$-67.96 + 0.0634T$ ± 0.3	4700 - 4.39T	1200 - 1500
0.330	0.278	$-63.81 + 0.0524T$ ± 0.7	4420 - 4.04T	1190 - 1500

* All temperatures are in °K

† Line determined by least square method, σ = standard deviation‡ Calculated from $\Delta\bar{G}_{Cr} = -3EF$

TABLE XI

Thermodynamic Properties of Cr in Solid Fe-Ni-Cr Alloys Determined
Directly from Cell Potentials*

x_{Cr}	x_{Ni}	T(°C)	E(mv)	$a_{Cr}^{\dagger}$	$\gamma_{Cr}^{\dagger}$	$-\Delta\bar{G}_{Cr}^{\#}$	$\Delta\bar{G}_{Cr}^{xs\#}$
0.087	0.070	900	53.92	0.202	2.322	3730	1960
		1000	64.13	0.173	1.988	4440	1740
		1100	74.35	0.152	1.747	5140	1520
		1200	84.56	0.135	1.552	5850	1290
0.090	0.154	900	50.11	0.226	2.511	3470	2145
		1000	60.50	0.191	2.122	4190	1900
		1100	70.88	0.166	1.844	4910	1670
		1200	81.26	0.146	1.622	5620	1416
0.095	0.287	900	48.35	0.238	2.505	3350	2140
		1000	58.01	0.204	2.147	4010	1930
		1100	67.68	0.180	1.895	4680	1750
		1200	77.35	0.160	1.684	5350	1525
0.204	0.072	900	23.45	0.498	2.441	1620	2080
		1000	31.11	0.427	2.093	2150	1870
		1100	38.78	0.374	1.833	2680	1650
		1200	46.44	0.334	1.637	3210	1440
0.202	0.173	900	21.24	0.532	2.634	1470	2260
		1000	28.80	0.455	2.252	1990	2050
		1100	36.37	0.398	1.970	2520	1850
		1200	43.93	0.354	1.752	3040	1640

TABLE XI (continued)

X_{Cr}	X_{Ni}	T(°C)	E(mv)	$a_{Cr}^{\dagger}$	γ_{Cr}	$-\Delta\bar{G}_{Cr}^{\#}$	$\Delta\bar{G}_{Cr}^{xs\ddagger}$
0.199	0.288	900	18.51	0.577	2.899	1280	2480
		1000	26.49	0.484	2.432	1830	2250
		1100	34.47	0.417	2.095	2380	2020
		1200	42.45	0.366	1.839	2940	1780
0.319	0.172	900	6.47	0.825	($\alpha+\gamma$)	448	($\alpha+\gamma$)
		1000	12.82	0.704	two-phase alloy	887	two-phase alloy
		1100	19.16	0.615		1330	
		1200	25.51	0.547		1770	
0.338	0.278	900	4.66	0.871	2.592	326	2220
		1000	10.50	0.750	2.232	727	2030
		1100	16.34	0.661	1.967	1130	1845
		1200	22.18	0.592	1.762	1530	1660

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

$\dagger \pm 2\%$

$\#$ In cal/g-mole

$\ddagger$ In cal/deg/g-mole

TABLE XII

Comparison of Measured and Calculated emf for
the Cell $\text{Fe-18Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-Y}_{0.5} | \text{Fe-30Cr, Cr}_2\text{O}_3$ at 1250°C

C E L L	E(mv)
1. $\text{Fe-18Cr, Cr}_2\text{O}_3 \text{S.O.E.} \text{Cr, Cr}_2\text{O}_3$; measured	60.20
2. $\text{Cr, Cr}_2\text{O}_3 \text{S.O.E.} \text{Fe-30Cr, Cr}_2\text{O}_3$; measured	37.90
3. $\text{Fe-18Cr, Cr}_2\text{O}_3 \text{S.O.E.} \text{Fe-30Cr, Cr}_2\text{O}_3$; ^{calculated} from 1&2	22.30
4. $\text{Fe-18Cr, Cr}_2\text{O}_3 \text{S.O.E.} \text{Fe-30Cr, Cr}_2\text{O}_3$; measured	21.10

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1. O-ring joint assembly
2. Ground glass joint
3. Gas inlet and outlet
4. Wax seal
5. Electrode lead wire (Pt-10%Rh)

6. Thermocouple (Pt/Pt-10Rh)
7. Glass-mullite seal
8. Mullite tube
9. Mullite support tube
10. Electrode
11. Electrolyte

12. Alumina push rod
13. Mullite tube
14. Zirconia support pallet
15. Compression spring
16. Tension spring

Fig 1

Fig 2

Fig 4

Fig 5

Fig 6

Fig 1

Fig 8

Fig 9

Fig 10

4/24/11

Fe-Cr alloy

Cr_2O_3

Fe-Cr alloy

(a)

(b)

Fig 12

Cr_2O_3

Fe-Ni-Cr alloy

(a)

(b)

(c)

Fig 13