255
8-25-81
(2)

(2)

DR-2970
B6679

ornl

ORNL-5781

MASTER

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

The Effect of Microstructure
on the Susceptibility of Low-Alloy
Steels to Hydrogen Attack

R. O. Williams

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Fossil
Energy
Program

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A04 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL-5781
Distribution
Category UC-90h

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

THE EFFECT OF MICROSTRUCTURE ON THE SUSCEPTIBILITY OF
LOW-ALLOY STEELS TO HYDROGEN ATTACK

R. O. Williams

Date Published: August 1981

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
U.S. DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

CONTENTS

ABSTRACT	1
INTRODUCTION	1
THE MECHANISM OF HYDROGEN ATTACK	2
THERMODYNAMIC FORMULATION	3
RELATION BETWEEN CARBIDE GROWTH AND CARBON ACTIVITY	7
EXPERIMENTAL	8
RESULTS	12
DISCUSSION	14
CONCLUSIONS	16
ACKNOWLEDGMENTS	16
REFERENCES	16
APPENDIX A	19
APPENDIX B	29

THE EFFECT OF MICROSTRUCTURE ON THE SUSCEPTIBILITY OF LOW-ALLOY STEELS TO HYDROGEN ATTACK

R. O. Williams

ABSTRACT

In an alloy steel in which one or more alloy additions stabilize the carbide phase, the carbon activity depends on the microstructure and the prior thermal history. The carbon activity is a major factor in the susceptibility of such steels to form internal methane bubbles when heated in high-pressure hydrogen. Thus one can expect to vary the susceptibility to hydrogen attack of a given steel by its prior treatment. The problem has two aspects. First, one needs to be able to calculate the equilibrium carbon activity when the steel is in internal equilibrium. A computer program in the appendix of this report takes care of part of this problem. When the thermodynamics of the mixed carbide phase is adequately modeled, then this problem can be solved. The second part is the rate of approach to equilibrium. An analysis of the rate of coarsening of carbides in such steels shows that this rate is enhanced by a fine carbide dispersion. Such a fine dispersion is also desirable for the maximum strength. Thus, we believe that under favorable circumstances the resistance to hydrogen attack can be enhanced by suitable thermal treatments of the steels used for the pressure vessels for hydrogen service.

INTRODUCTION

Low-alloy steels are degraded when exposed to hydrogen at elevated pressures and temperatures. This was originally discovered in the early days of the synthetic ammonia industry and later in the petrochemical industry. It is also a potential problem in future coal processing plants. What happens is that hydrogen diffuses into the steel and reacts with carbon to form methane bubbles at the internal interfaces. The surface decarburizes somewhat, but the presence of the bubbles is primarily responsible for the loss of strength and ductility.

It has been known for many years that the use of alloy steels reduces or eliminates this problem, and it was recognized later that this was because the alloy additions increase the stability of the carbides, reducing the activity of carbon and hence the potential for methane

formation. However, because such alloy steels are more expensive and more difficult to fabricate, one desires to use the lowest alloy content that will give the desired service life.

Steels are not generally in internal equilibrium. Thus, the carbon activity will depend on the microstructure and the thermal history. Our primary effort is to look into the possibility of enhancing the resistance to attack by suitably selecting the starting structure. The problem has two parts. First, we have to understand the thermodynamics of the alloy systems, and then we must consider the rate at which internal equilibrium is approached.

THE MECHANISM OF HYDROGEN ATTACK

At elevated temperatures hydrogen readily diffuses into the steel. There is a potential for the reaction of the hydrogen with the carbon in solution and in the carbide phase, but no reaction takes place because the methane cannot be contained in the lattice. However, if a minute void or other singularity exists, then the hydrogen and the carbon react at the void surface to form methane, which fills the void. Because of the high methane pressure, the void will grow into a microscopic bubble; the process can be so extensive that the volume of the sample may increase 10%. The bubbles occur primarily on the internal boundaries.

In Fig. 1 we show schematically how the process works. In Fig. 1(b) we represent the stresses on a cut through the boundary. A positive stress due to the methane pressure is balanced by the interfacial energy and the tensile stress in the boundary. It is apparent that this process has a number of steps, but Shewmon¹ has concluded that the rate of growth is normally controlled by the diffusion of the iron atoms in the boundary due to the stress gradient. As the bubble diameter increases the rate accelerates rapidly because the stress is proportional to the square of the bubble diameter. Thus, the process is characterized by exhibiting no apparent change for an extended period and then a relative rapid increase in volume. However, recently some strain measurements of very high sensitivity have detected changes early in the process.² Thus, our simple picture may require some refinement.

Fig. 1. The formation of methane bubbles at internal boundaries. The carbon and hydrogen diffuse to the surface of the bubble, where they react to form the methane (a). The methane pressure is balanced by the surface tension of the bubble plus the tensile stress induced in the matrix (b). The rate of growth of the bubbles is controlled by the diffusion of the iron atoms along the boundary due to the stress gradient.

THERMODYNAMIC FORMULATION

For the reaction

we can calculate the equilibrium methane pressure as

$$P_{\text{CH}_4} = A_{\text{C}} P_{\text{H}_2}^2 e^{-G/RT}, \quad (2)$$

where

- G = the free energy for the reaction,
- P_{H_2} = the hydrogen pressure,
- A_{C} = the carbon activity.

The process is seen to depend strongly on the hydrogen pressure, a direct result of the fact that each methane molecule contains two hydrogen molecules. The free energy for the reaction is negative at low temperatures and becomes zero around 600°C. This in part accounts for the ability of comparatively small alloying additions to substantially increase the resistance to hydrogen attack.

Consider how alloying influences the carbon activity and how this activity may be changed by suitable heat treatment. Except at the highest temperatures the carbide as initially formed will contain the same proportion of metallic elements as exists in the parent alloy. This compositional relation is represented in Fig. 2, and the carbon activity is given by the construction in Fig. 3. Thus, if we have an adequate representation of the thermodynamics of the alloyed ferrite and the carbide, then we can calculate the initial carbon activity.

Alloying additions that contribute to the stability of the carbide will begin to partition to the carbide when the alloy is held at sufficiently high temperatures. This is represented by the shifting tie line as shown in Fig. 4. The construction that now represents the carbon

Fig. 2. Low-temperature phase diagram of the iron-chromium-carbon system. The carbide as initially formed contains the metallic elements in the same proportions as the alloy, as shown by the direction of the non-equilibrium tie line.

Fig. 3. Schematic representation of carbon activity along the tie line of Fig. 2. Parabolalike curves represent the activity in ferrite and cementite $[(\text{Fe},\text{Cr})_3\text{C}]$. Extrapolating the common tangent to pure carbon gives the initial carbon activity.

Fig. 4. Phase diagram showing effect of higher temperatures on carbon behavior. At temperatures high enough that metal atoms can diffuse, chromium, and molybdenum are selectively partitioned to the carbide phase, so the tie line of Fig. 2 rotates toward the equilibrium position.

activity is more complex but can be represented by taking the free energy along a section of the diagram that includes pure carbon. There is one section for the ferrite and a second for the carbide. The carbon is much more mobile than the alloying additions, and hence the carbon activity in

both phases will be the same, as shown in Fig. 5. Thus, we can calculate the carbon activity as a function of the partitioning if we have adequate thermodynamic models. This construction represents the alloys as a ternary system, whereas most alloys contain both chromium and molybdenum. With four components one can no longer represent geometrically the construction that determines the activity, but the activity still can be calculated.

According to the analysis of Verugopalan and Kirkaldy³ and the equations given here one can calculate the time required for the partitioning to be completed. It remains to be seen if such calculations support our experimental results that show enhanced resistance for our combinations of microstructures and thermal histories.

Fig. 5. Schematic representation of free energy versus composition for the ferrite and the carbide phase along the two dashed lines that pass through the ends of the tie line in Fig. 4. Because the carbon is much more mobile than the chromium or molybdenum the carbon activity will be the same in both phases. Appendix B gives a computer program that permits one to calculate the thermodynamic properties of the ferrite. When the thermodynamics of the carbide phase is determined one can calculate the initial carbide activity as well as the activity versus the degree of partitioning.

RELATION BETWEEN CARBIDE GROWTH AND CARBON ACTIVITY

This section considers the time dependence of the carbon activity. The steels normally used for service where hydrogen attack is a problem contain up to 3% Cr and 1% Mo. The carbon is the primary strengthening agent and 0.1% may be present. When such steels are heated to around 900°C, they become completely austenitic, with all the carbides in solution. The structure obtained on cooling depends critically on the cooling rate. For a modest rate primary ferrite forms first and then relatively coarse pearlite. Faster cooling reduces the amount of ferrite and gives a finer pearlite. Still faster cooling rates can avoid the formation of ferrite and pearlite completely, and bainite may form; the lower the temperature at which it forms, the finer is the carbide dispersion.

If still faster cooling can avoid bainite, then the steels will transform to martensite. Martensite structures are tempered to enhanced toughness, and this gives a very fine carbide dispersion.

It is well known that alloying additions retard the growth of the carbide particles. This is why alloy steels have higher elevated-temperature strengths than unalloyed steels of similar carbon contents. This retarding effect is associated with the partitioning of the alloy additions to the carbide phases such that growth now requires the diffusion of both carbon and the alloying additions. As we saw in the last section, this partitioning also controls the carbon activity. Recently Venugopalan and Kirkaldy³ have analyzed in detail the coarsening of the carbides in which the rate is controlled by the diffusion of the alloy additions. Further, the analysis includes the effect of diffusion along dislocations, which is very important at low temperatures for structures derived from martensite and bainite. They have derived the rate equation

$$\frac{dr}{dt} = KD^* r^{-2}, \quad (3)$$

where

K = a defined constant;

- r = the average radius of the carbide particles;
 D^* = an effective diffusion coefficient, which was given in terms of the partitioning of the alloy elements.

Their analysis assumes that essentially equilibrium partitioning is taking place such that when perceptible growth, say

$$\Delta r/r \geq 0.1, \quad (4)$$

has taken place the partitioning should be essentially complete. The time required is then given as

$$\Delta t \geq 0.1r^3/D^*K. \quad (5)$$

This shows the great importance of having a fine carbide dispersion to minimize the equilibration time. The temperature dependence of D^* is less than for bulk diffusion because of the diffusion along the dislocations.

EXPERIMENTAL

The previous sections have analyzed how the susceptibility to hydrogen attack should depend on alloy content and heat treatment. We cover certain additional aspects of the problem and our experimental program in this section.

The computer program explained in Appendix A and given in Appendix B gives a state-of-the-art representation of the thermodynamics of the alloys containing up to 13 components, including those of interest in this program. Thus, we believe that we have an adequate representation of the thermodynamics of the ferrite. There is some information on the stability of the carbide phases in the Fe-Cr-C and Fe-Mo-C ternary systems, which will, we believe, allow us to adequately define the thermodynamics of the carbide in which some of the iron is replaced with chromium and molybdenum, but this remains to be done. The calculations of this constrained equilibrium, from which the carbon activity can be determined, will require an additional computer program.

Ideally one would like to actually measure the carbon activity, but this does not appear feasible at the temperatures of interest to us. However, it can be measured at higher temperatures. The time dependence of the carbon activity has been established at 650°C in 2 1/4 Cr-1 Mo steel.⁴

The steel we used was grade SA-335 P 11 in the form of an approximately 0.3-m-ID (12-in.) pipe having a 25.4 mm (1 in.) wall. This material was kindly supplied by Babcock and Wilcox through the efforts of Jack Lange. This material contained 1.25 Cr, 0.5 Mo, and 0.10 C (wt %).

Samples (12.7 by 12.7 by 38 mm) were cut from the pipe and were austentized at 927°C (1700°F) for 30 min. One set of samples was quenched in water, a second set was cooled at 4.4°C/s (8°F/s), and a third at 28°C/min (50°F/min). These treatments were selected to give the widest possible range of starting structures. The resulting microstructures are shown in Figs. 6 through 8. Part of the samples from each set were given an additional anneal for 48 h at 625°C (1160°F). While this anneal is sufficient to produce internal changes in the samples, it does not result in significant changes in the microstructure as revealed by optical microscopy.

Fig. 6. Microstructures of sample held at 927°C for 30 min and water quenched.

Fig. 7. Microstructure of sample held at 927°C for 30 min and cooled at 4.4°C/s through the transformation range.

Fig. 8. Microstructure of sample held at 927°C for 30 min and cooled at 28°C/min through the transformation range.

The apparatus shown in Fig. 9 was used to expose the samples to high-pressure hydrogen at elevated temperatures. It consisted of a commercial stainless steel autoclave placed partway into a muffle furnace. By insulating the exposed part of the autoclave wall and putting additional insulation inside to eliminate the hydrogen convection currents, we could minimize the temperature difference between the furnace and the samples inside the autoclave. Because trace impurities in the hydrogen cannot influence the reaction taking place inside the samples, no purification of the tank hydrogen was required. The autoclave was flushed with argon as a safety measure before being flushed with hydrogen.

A high-temperature strain gage was welded to each sample to monitor the volume expansion during the runs. A reference gage was welded to a 2 1/4 Cr-1 Mo steel to compensate for temperature changes and drift (aging) in the strain gages. This aspect of the experiment did not prove overly successful because of extensive mechanical problems, which led to shorting or opening of the gage leads. Further, the drift was not completely compensated for, and also a gage might occasionally exhibit a sudden shift for unknown reasons. The volume changes that the samples experienced were small and occurred over such extended time periods that

Fig. 9. Sketch of our experimental setup.

they would tax the sensitivity of the method under more ideal circumstances. While such gages do show some promise in remotely monitoring volume changes during hydrogen attack, it is clear that considerably more development work is required.

The lengths of the samples before and after exposure were measured, but this also does not give an entirely satisfactory measure of the volume increase because the growth is not isotropic. The most sensitive and reliable results were obtained from density measurements using the displacement method, and only volume changes obtained by this method are reported here.

RESULTS

Some of our results are summarized in Table 1. We would interpret the magnitude of the degree of attack as indicated by the volume increases as follows. For the slowest cooling rates we assume that the chromium and molybdenum partitioned to the carbide phase reasonably completely and, thus, imparted an enhanced degree of resistance to attack. Hence, the additional anneal has no additional effect.

Table 1. Summary of response to hydrogen attack

Sample	Cooling ^a	Exposure				Decarburization		
		Temperature (°C)	Time (h)	Pressure		ΔV (%)	(mm)	(in.)
				(MPa)	(psi)			
1	Quenched	505	650	11.0	1600	0.30		
2	Quenched	535	1450	11.0	1600	0.33		
3	Quenched ^b	525	1870	11.0	1600	0.96		
4	4.4°C/s	535	1450	11.0	1600	0.26	0.03	0.001
5	4.4°C/s	520	1870	11.0	1600	1.16	0.03	0.001
6	4.4°C/s ^b	520	1870	11.0	1600	0.01	0.03	0.001
7	28°C/min	490	430	11.4	1650	0	0.58	0.023
8	28°C/min	535	1450	11.0	1600	0.06	0.56	0.022
9	28°C/min ^b	525	1870	11.0	1600	0.14	5.1	0.20

^aAfter holding 30 min at 927°C. Quench is in water.

^bFollowed by 48-h anneal at 625°C.

For the intermediate cooling rate the degree of partitioning was so greatly reduced that the attack was greater. The subsequent anneal provided the partitioning and drastically reduced the degree of attack.

For the fastest cooling rate, the partitioning would have been essentially zero, but in this case the degree of dispersion is believed to be so fine that partitioning took place during exposure so that the attack was somewhat less compared with the intermediate cooling rate.

Occasionally, blisters form as a result of separation along oxide stringers and give abnormally large volume increases. Normally this condition can be spotted by visual examination, but this need not be true if the blister is too far removed from the surface. We believe that this accounts for the anomolous behavior for Sample 3, but this has to be looked into more carefully.

We have used an earlier version of the program in Appendix B to estimate the equilibrium carbon activity in the steels of interest to this program and have further assumed that each steel will exhibit attack at the same methane potential [from Eq. (1)]. This allowed us to extrapolate the Nelson curve for a plain carbon steel to obtain the curves for the alloys. Our results are shown in Fig. 10. These results are based upon a

Fig. 10. Calculated Nelson curves for alloy steels. The equilibrium carbon activity was estimated for various steels. We assumed that hydrogen attack would occur at the same partial pressure of methane such that the plain carbon curve, the lowest curve, is shifted to give an estimated curve of each alloy steel.

less reliable set of thermodynamic parameters as well as certain other approximations and are not to be considered highly accurate. However, we do believe that they establish that the concept that the attack occurs at essentially the same methane potential (at a given temperature) is valid.

DISCUSSION

The literature has often stated that the volume change that occurs during hydrogen attack remains very small for an extended period of time and then starts to increase rather rapidly. The volume increase in our samples apparently occurred more gradually. This materially complicated the attempts to monitor the dimension changes with the strain gages, which were subject to drifts and instabilities.

Our volume changes, which are reported in Table 1, support in a general way the effect of microstructure and prior history on the resistance to hydrogen attack. A complete microstructural study to detect internal blisters and assess the uniformity of the attack has not yet been carried out. Ideally, it would be useful to determine the sizes and densities of the bubbles, but this can be difficult because of their small size.

As seen in Table 1 and in Figs. 11 and 12, the degree of decarburization does not appear to correlate with the resistance to hydrogen attack. Why this should be remains to be established. The problem is in part experimental in that optical microscopy is not capable of detecting any but the largest methane bubbles, and thus we presently have no information about the density of bubbles in the various samples. We expect to address this question using scanning electron microscopy. Another question is whether or not another carbide, in addition to cementite, has formed for the samples having very fine carbide dispersions.

Fig. 11. A quenched samples heated at 535°C for 1450 h in hydrogen at 11.0 MPa (1600 psi) showing no apparent change in microstructure (sample 2 in Table 1).

Fig. 12. A sample cooled at 28°C/min exposed to hydrogen at 11.0 MPa (1600 psi) at 535°C for 1450 h showing extensive decarburization (sample 8 in Table 1).

CONCLUSIONS

1. The enhanced resistance to hydrogen attack of alloy steels arises from the reduction in the carbon activity as a result of forming carbides that are thermodynamically more stable.

2. Such steels are not generally in internal equilibrium in that the partitioning of the alloying additions to the carbides is not complete. This partitioning is required to give the more stable carbide. Thus it follows that the carbon activity is sensitive to the microstructural and thermal history.

3. From an analysis available in the literature, it should be possible to predict the degree of partitioning as a function of thermal history for a given carbide dispersion. In particular, a fine carbide greatly favors rapid partitioning.

4. Although our analysis is incomplete, our results have shown that the degree of hydrogen attack is sensitive to the microstructure in qualitative agreement with the analysis.

5. These results provide a direction for the specification of treatments to give maximum resistance to attack. Specifically, any structure that can be tempered to a sufficiently high temperature to give carbide growth should approach the minimum carbon activity.

ACKNOWLEDGMENTS

The manuscript was reviewed by J. M. Leitnaker and R. E. Funderlic, edited by S. Peterson, and prepared for publication by A. F. Rice.

REFERENCES

1. P. G. Shewmon, "Hydrogen Attack of Carbon Steel," *Metall. Trans. A* 7A: 279-86 (1976).
2. G. Sundararajan and P. G. Shewmon, "The Hydrogen Attack of HSLA Steels," *Metall. Trans. A* 11A: 509-16 (1980).

3. D. Venugopalan and J. S. Kirkaldy, "New Relations for Predicting the Mechanical Properties of Quenched and Tempered Low Alloy Steels," pp. 249-67 in *Hardenability Concepts with Applications to Steel*, D. V. Doane and J. S. Kirkaldy, eds., The Metallurgical Society of AIME, Warrendale, Pa., 1978.
4. K. Natesan and T. F. Kassner, "Monitoring and Measurement of Carbon Activity in Sodium Systems," *Nucl. Technol.* 19: 46-57 (1973).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX A

Thermodynamic Formulation

In Appendix B we give a computer program complete with data deck and some results. The program is used to calculate the free energy and the activities of each component for alloys composed of up to 13 components and forming a liquid, body-centered cubic, face-centered cubic, or hexagonal close-packed solid solution. This appendix gives the thermodynamic formulation of the program along with instructions for its use.

The parameters on which the program is based were derived by Kaufman and co-workers¹⁻⁷ and were obtained from the referenced sources. The collection covers binary pairs of C, Al, Si, Ti, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, and W, although not all pairs are fully represented yet.

We represent the free energy of a solution as

$$G = \sum X_i G_i + RT \sum X_i \ln X_i + \sum X_i X_j [U + V(X_j - X_i)] , \quad (A1)$$

in the present formulation. The first sum represents the contribution when the structure of the solution does not correspond to that of the standard state of the i th component. The second sum is the ideal entropy of mixing. In the final sum, which is taken over all possible pairs, the part represented by U is a regular solution model, whereas the V component represents the asymmetry. The formulation of the asymmetry is different from the usual formulation; the reason for this modification has been covered elsewhere.⁸

In the original source of the parameters the enthalpy (heat of mixing) and the excess entropy were given separately. However, we are interested only in the free energy and have combined these functions according to the standard thermodynamic formulation

$$G = H - TS . \quad (A2)$$

For a pure component, the presentation is always of the form:

$$G_i = a + bT + cT^2 + dT^3 + eT^4 . \quad (A3)$$

The number of terms required depends on the complexity of the difference in specific heat between the structure and the standard state. Most of the components are represented by only two terms.

The solutions for the binary systems that are presently represented in the data set have been represented by four different expressions. The first is given as

$$G_{ij}^E = X_i X_j [X_i(a + bT) + X_j(c + dT)] , \quad (A4)$$

such that our parameters are given as

$$U = [a + c + (b + d)T]/2 , \quad (A5)$$

and

$$V = [c - a + (d - b)T]/2 . \quad (A6)$$

In the second case the expression is given as

$$\begin{aligned} G_{ij}^E = X_i X_j [X_i(a + bT) + X_j(c + dT) \\ + (e + fT)(X_i - X_j)^2 + (g + hT)(X_i - X_j)^3] , \end{aligned} \quad (A7)$$

but we have dropped the last two terms, so U and V are still defined as in Eqs. (A5) and (A6).

In the third case, where

$$G_{ij}^E = X_i X_j [X_i(a + bT) + X_j(c + dT) + eT^2 + fT^3 + gT^4] , \quad (A8)$$

U is now defined as

$$U = [a + c + (b + d)T]/2 + eT^2 + fT^3 + gT^4 , \quad (A9)$$

and V remains unchanged.

The final case is represented as

$$\begin{aligned} G_{ij}^E = & X_i X_j [X_i (a + bT + cT^2 + dT^3) \\ & + X_j (e + fT + gT^2 + hT^3)] \end{aligned} \quad (\text{A10})$$

where U and V now become

$$U = [a + e + (b + f)T + (c + g)T^2 + (d + h)T^3]/2, \quad (\text{A11})$$

and

$$V = [e - a + (f - b)T + (g - c)T^2 + (h - d)T^3]/2. \quad (\text{A12})$$

The different cases are identified in our computer program by the variable IC, which has the values of 0, 1, 2, and 3, respectively. The first case is most commonly used; there are 14 instances of the fourth case and one each of the second and third. For the present data set the neglect of the higher order terms for case 2 is of consequence only if we are considering bcc alloys containing substantial amounts of both copper and iron.

The partial free energy for the i th component is given as

$$\begin{aligned} \bar{G}_i = & G_i + RT \ln X_i + \sum X_j \{ U(1 - X_i) - V[2X_i(1 - X_i + X_j) - X_i] \} \\ & - \sum X_j X_l [U + 2V(X_l - X_j)] . \end{aligned} \quad (\text{A13})$$

We see that all binary parameters contribute. As a verification that the partial free energies are correct, one can sum them, as

$$G = \sum X_i G_i, \quad (\text{A14})$$

to recover the total free energy, G .

The activity is given as

$$a_i = \exp(\bar{G}_i/RT). \quad (\text{A15})$$

Should one be interested, the entropy, the heat of mixing, and the excess specific heat can be obtained from the standard operations

$$S = \frac{dG}{dT},$$

$$H = G + TS, \quad (A16)$$

$$C_p = \frac{dH}{dT}.$$

The partial quantities can be similarly obtained.

Standard States

All the calculations of the program use a single crystalline form for each element as the reference state. If only one crystalline form normally exists then this is, of course, the reference state. Otherwise, the form that exists over the widest temperature range is the standard state. Specifically, the standard states are as follows:

<u>Element</u>	<u>Standard State</u>
C	Graphite
Al	fcc
Si	Diamond cubic
Ti	bcc
Cr	bcc
Mn	α -Mn
Fe	bcc
Co	fcc
Ni	fcc
Cu	fcc
Nb	bcc
Mo	bcc
W	bcc

Program Design

This program consists of a main program, THERMO, which calls the following subroutines: ELEMENT, COVER, ALLOY, TOTAL, and PARTIAL. By

this particular arrangement, most of the changes that are required in going to a different or larger set of elements can be made in the main program. Also, by changing the calling statements in this program one can restrict the calculations to only those desired. Further, additional modifications can be similarly handled as subroutines. The call ZERO is a library routine, which initially sets the specified variables to zero. As used it sets labeled commons A through I to zero. It is mandatory that INDEX be set to zero for the program to work correctly.

Routine ELEMENT verifies that certain input data are correct.

Routine LIST called by ELEMENT reads in the thermodynamic parameters. Each card is identified by the chemical symbols, which occupy the first four columns, and the phase in the next three. The standard chemical symbols are used, and if the symbol is a single letter it goes in the first or third column. When the data are for a pure component the symbol is repeated. When two cards are required the enthalpy is always first and is identified by H in the eighth column, and the entropy by S, but no check for this order is built into the program. The values of IC are given in the ninth column. One can establish this formatting of the input data by comparing the literature values with the output of LIST.

The computations for the free energy require that the i th element come before the j th, the position being defined by the table generated in ELEMENT. It is possible to include parameters for the same system more than once in the deck. The duplicate sets are flagged, and only the final set is used in the computations. Thus, one can make trial substitutions by simply adding the additional cards at the end of the data cards. The end of the data deck is signaled by having IC = 9.

LIST prepares a complete list of the free energy equations. If one wishes to suppress this output in part or completely, this can be done by adjusting the variable IPT.

Even if the parameters have values of zero, it is important that the data cards still be included so that these values are recorded. As the program is written, missing values are, in effect, taken to be zero.

The routine COVER makes a list of the structures for which parameters have been included. The numbers identify the locations of the parameters in the data deck. The use of this routine is optional.

Subroutine ALLOY normalizes the composition. If the value 1 is in column 5 on the composition card, the input data are taken to be in units of mass and composition is converted to atomic fractions.

Subroutine TOTAL calculates the total free energy by calling function GF. The partial free energy for each component for each solution as a function of temperature is calculated by calling PF. The total free energy is also given as

$$G = \sum X_i G_i, \quad (A17)$$

which is used to verify that the calculations are consistent.

Discussion

Considerable effort went into designing this program so that it can be used with different or additional data. It can also be expanded readily to include additional components. With one exception all the required changes are made in the main program. The maximum number of components is NUM, assigned in the main program. The location of the parameters for a given system is given by the value of INDEX(L), where

$$L = I + J \cdot \text{NUM} + K \cdot \text{NUM}^2 - \text{NUM} - \text{NUM}^2. \quad (A18)$$

When the number of components is not 13, the value of L will have to be redefined wherever it is used. The values of K are 1, 2, 3, and 4 for the liquid, bcc, fcc, and hcp structures, respectively. The identity of a particular element is given by the variable EL. In the present case these identities are listed in order of increasing atomic weights. Any order can be used, but the atomic weights, AT, must correspond. In defining L, I is less than or equal to J, the value of I and J being defined by the position in EL.

The data listed in the appendix were taken from Kaufman et al.¹⁻⁷ As circumstances permit, we will be glad to supply decks of this program, and the data deck will be hopefully updated as more parameters are published. Listing of the current sources should also be supplied.

As the present program is written, the calculations leave out missing data; this corresponds to having zero excess free energy for such binary pairs. In metallic systems, it is generally observed that the free energy of formation or mixing is not strongly structure dependent, so it would generally be better to use thermodynamic properties of one of the other solutions for such missing cases. As the number of components increases the heat effects become relatively less important compared with the entropy effects, so either of the above approximations might be satisfactory for complex systems.

From the partial free energies and the activities, one can estimate all kinds of interesting things, such as the rates of evaporation, solubilities in liquid metals, and the potential for reaction with foreign agents. The program can be used for other important calculations, as will be covered briefly here. The special case for the changing carbon activity in alloy steels was covered in the body of the report.

We have calculated the free energy versus temperature for the liquid and the bcc and fcc solid solutions of an Fe-base alloy containing 16 Cr, 8 Ni, and 2 Mo (wt %). This is the basic composition of an alloy used for welding. As is seen in Fig. A1, the fcc phase is stable up to 1260°C and

Fig. A1. The calculated free energy for the liquid and the bcc and fcc solid solutions for an Fe-base alloy containing Cr, Ni, and Mo. The curvature of the fcc free energy is due to the temperature dependence of the free energy of fcc Fe.

then the liquid phase is stable. The point of intersection of these curves falls within the liquid-solid two-phase field. An actual calculation of the equilibrium between these two phases (Fig. A2) shows that this composition exhibits a very limited solidification range (which is important in welding). This figure also shows that a mixture of bcc and fcc phases is stable below 700°C. There are two points to be considered in this regard. At this temperature the formation of bcc phase would be fairly slow; further, the presence of any carbon or nitrogen would strongly stabilize the fcc phase. There is very little difference in composition between the liquid and solid other than that the concentration of molybdenum in the liquid is about 5 times that in the fcc phase. Below 700°C the nickel partitions rather strongly to the fcc phase but the molybdenum partitions less strongly to the bcc phase.

Fig. A2. The calculated phase diagram for the alloy of Fig. A1. There is a limited freezing range, in which the liquid and fcc phase are similar in composition except that the molybdenum partitions to the liquid. According to these calculations the fcc phase would precipitate a bcc phase. The nickel partitions to the fcc phase, the molybdenum to the bcc phase.

These particular calculations were done on a TRS-80. This program is not presently compatible with the program documented in this report.

Ultimately, one desires to calculate the equilibrium between the solution phases and possible intermediate phases. Kaufman and associates have furnished the required information of the binary intermediate phases, so what is now required is a computer program that uses the present program and this additional data and calculates the equilibrium phases. However, the situation can become complex when the intermediate phases contain three or more components.

References

1. L. Kaufman, "Proc. 4th CALPHAD Meeting, Workshop on Computer Based Coupling of Thermochemical and Phase Diagram Data," *CALPHAD* 1(1): 7-89 (1977).
2. L. Kaufman and H. Nesor, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - I," *CALPHAD* 2(1): 55-80 (1978).
3. L. Kaufman and H. Nesor, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - II," *CALPHAD* 2(1): 81-108 (1978).
4. L. Kaufman, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - III," *CALPHAD* 2(2): 117-46 (1978).
5. L. Kaufman and H. Nesor, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - IV," *CALPHAD* 2(4): 295-318 (1978).
6. L. Kaufman and H. Nesor, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - V," *CALPHAD* 2(4): 325-348 (1978).
7. L. Kaufman, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - VI," *CALPHAD* 3(1): 45-76 (1979).
8. R. O. Williams and J. Brynestad, "Solution Models - A New Perspective," paper in preparation.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

APPENDIX B

Computer Program, Input Data, and Partial Listing of Output

If the program is run by using the listed input data thru page 41 then one should generate the output on the following pages.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

```

PROGRAM THERMO
C A PROGRAM TO CALCULATE THE THERMODYNAMIC PROPERTIES OF ALLOYS COMPOSED OF
C C, AL, SI, TI, CR, MN, FE, CO, NI, CU, NB, MO, AND W USING PARAMETERS
C FROM THE WORK OF KAUFMAN AND NESOR. 1981
C ROBIN WILLIAMS, METALS AND CERAMICS, OAK RIDGE NATL LAB, OAK RIDGE, TENN.
C NUM = DATA SETS, T = K, M, N = BINARY PAIR, IND = NO. OF COMPONENTS, AT =
C ATOM WEIGHT, EL = ATOM SYMBOL, PH = LIQ, BCC, FCC, HCP, W = COMPOSITION AS
C WEIGHT FRACTION, X = ATOM FRACTION
COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V$COMMON/Z/IQD(676)
IND=13$CALLZERO(A,(8*300+IND**2*4)*4)
CALLELEMENT$CALLCOVER$DO1I=1,10$CALLALLOY$CALLTOTAL
1 CALLPARTIAL$END

```

```

SUBROUTINEELEMENT
C THIS PROGRAM VERIFIES NAMES, STANDARD STATES AND ATOMIC WEIGHTS
COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V
READ100,EL,PH,TH,IS$READ101,AT$PRINT102
DO1I=1,IND$J=IS(I)$IF(J.EQ.0)J=5
1 PRINT103,I,EL(I),AT(I),PH(J)$CALLLIST$RETURN
100 FORMAT(13A2,5A3,3A1,13I1)
101 FORMAT(13F5.2)
102 FORMAT(40H1 ELEMENT AT WEIGHT STD STATE,/)
103 FORMAT(I10,5X,A2,F10.2,7X,A3)$END

```

```

SUBROUTINELIST
COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V
PRINT104$IPT=3$DO1IA=1,900
READ100,U,V,Y,Z,IZ,A1,A2,A3,A4,A5,A6

```

```

      PRINT110, IZ
      IF (IZ.EQ.9) GOTO100$IZ=IC (IA) =IZ+1
      IF (XX.NE.U.OR.YY.NE.V) PRINT101$XX=U$YY=V
      N=M=J=K=L=0$IPT=IPT+1$DO9I=1, 13$IF (U.EQ.EL (I) ) M=I
      IF (V.EQ.EL (I) ) GOTO5
9  CONTINUE
5  N=I$DO11I=1, 4
11 IF (PH (I) .EQ.Y) K=I
    IF (M.GT.0.AND.N.GT.0.AND.K.GT.0) GOTO8$PRINT109$GOTO1
8  J=M+N*13+K*169-182
    JJ=INDEX (J) $INDEX (J) =IA$IF (JJ.NE.0) PRINT108,JJ
    IF (M.EQ.N) GOTO10$GOTO (20, 31, 42, 53) IZ
10 A (IA) =A1$B (IA) =A2$C (IA) =A3$D (IA) =A4$E (IA) =A5
    IF (IPT.LT.1) GOTO1$PRINT110, IA, Y, V, A1, A2$IF (A3.EQ.0.) GOTO1
    PRINT111, A3$IF (A4.EQ.0.) GOTO1$PRINT112, A4$IF (A5.EQ.0.) GOTO1
    PRINT113, A5$GOTO1
20 A3=-A3$A4=-A4$D (IA) = (A4-A3) /2.
    A (IA) = (A1+A2) /2.$B (IA) = (A3+A4) /2.$C (IA) = (A2-A1) /2.
    IF (IPT.GT.0) PRINT120, IA, PH (K) , U, V, U, A1, A3, V, A2, A4$GOTO1
31 READ100, U, V, Y, Z, IB, B1, B2, B3, B4, B5, B6
    B1=-B1$B2=-B2$B3=-B3$B4=-B4$D (IA) = (B2-B1) /2.
    A (IA) = (A1+A2) /2.$B (IA) = (B1+B2) /2.$C (IA) = (A2-A1) /2.$IF (IPT.GT.0)
1PRINT131, IA, Y, U, V, U, A1, B1, V, A2, B2, A3, B3, U, V, A4, B4, U, V$GOTO1
42 READ100, U, V, Y, Z, IB, B1, B2, B3, B4, B5, B6
    B1=-B1$B2=-B2$B3=-B3/2.$B4=-B4/3.$B5=-B5/4.
    A (IA) = (A1+A2) /2.$B (IA) = (B1+B2) /2.$C (IA) = (A2-A1) /2.
    D (IA) = (B2-B1) /2.$E (IA) =B3$F (IA) =B4$G (IA) =B5
    IF (IPT.GT.0) PRINT142, IA, Y, U, V, U, A1, B1, V, A2, B2, B3, B4, B5$GOTO1
53 READ100, U, V, Y, Z, IB, B1, B2, B3, B4, B5, B6
    B1=-B1$B2=-B2/2.$B3=-B3/3.$B4=-B4$B5=-B5/2.$B6=-B6/3.
    A (IA) = (A1+A4) /2.$B (IA) = (B1+B4) /2.$C (IA) = (B2+B5) /2.
    D (IA) = (B3+B6) /2.$E (IA) = (A4-A1) /2.$F (IA) = (B4-B1) /2.
    G (IA) = (B5-B2) /2.$H (IA) = (B6-B3) /2.
    IF (IPT.GT.0) PRINT153, IA, Y, U, V, U, A1, B1, B2, B3, V, A4, B4, B5, B6
1  CONTINUE
100 NUM=IA-1$RETURN
100 FORMAT (2A2, A3, A1, I1, X, 2 (F10.0, 2E10.0))

```

```

101 FORMAT(1H )
104 FORMAT(///,10X,39H LISTING OF THE FREE ENEEGY EXPRESSIONS,/)
108 FORMAT(45H      SYSTEM/STRUCTURE PREVIOUSLY DATA SET NO. ,I4)
109 FORMAT(55H      SOME PROBLEM IN THIS CARD *****)
110 FORMAT(I4,3X,A3,2X,A2,5H G = ,F9.0,2H + ,F9.2,2H*T)
111 FORMAT(1H+,42X,2H+ ,E10.4,5H*T**2)
112 FORMAT(1H+,62X,2H+ ,E10.4,5H*T**3)
113 FORMAT(1H+,82X,2H+ ,E10.4,5H*T**4)
120 FORMAT(I5,2X,A3,5H G = ,2A2,2H( ,A2,1H(,F8.0,3H + ,F7.2,6H*T) + ,
1A2,1H(,F8.0,3H + ,F7.2,4H*T)) )
131 FORMAT(I5,2X,A3,5H G = ,2A2,1H(,2(A2,1H(,F8.0,1H+,F7.2,4H*T)+,),
11H(,F8.0,1H+,F7.2,4H*T) (,A2,1H-,A2,5H) **2+,1H(,F8.0
2,1H+,F7.2,4H*T) (,A2,1H-,A2,5H) **3) ,)
142 FORMAT(I5,2X,A3,5H G = ,2A2,1H(,2(A2,1H(,F8.0,3H + ,F7.2,5H*T) + )
1E10.4,8H T**2 + ,E10.4,7HT**3 + ,E10.4,5HT**4))
153 FORMAT(I5,2X,A3,5H G = ,2A2,1H(,A2,1H(,F8.0,1H+,F7.2,3H*T+,E10.4,
16H*T**2+,E10.4,7H*T**3)+,A2,1H(,F8.0,1H+,F8.2,3H*T+,E10.4,
26H*T**2+,E10.4,7H*T**3)) ,) $END

```

SUBROUTINECOVER

```

C  LISTS THE STRUCTURES FOR WHICH DATA HAVE BEEN PROVIDED
COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/LC(300)
2/H/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V
DIMENSIONPHI(4),NS(4),NP(250)$CALLZERO(NP,1000)
PRINT100$DO1I=1,IND$PRINT101$DO2J=1,IND$KK=0
DO3K=1,4$IF(J.LT.I)GOTO5$IX=INDEX(I+J*13+K*169-182)
IF(IX.EQ.0)GOTO3$KK=KK+1$PHI(KK)=PH(K)$NS(KK)=IX
NP(IX)=NP(IX)+1$GOTO3
5 IX=INDEX(J+I*13+K*169-182)$IF(IX.EQ.0)GOTO3$KK=KK+1
PHI(KK)=PH(K)$NS(KK)=IX$NP(IX)=NP(IX)+1
3 CONTINUE$IF(I.NE.J)PRINT102,EL(I),EL(J),(PHI(IJ),NS(IJ),IJ=1,KK)
2 IF(I.EQ.J)PRINT103,EL(I),(PHI(IJ),NS(IJ),IJ=1,KK)
1 CONTINUE$RETURN
100 FORMAT(///,10X,86HSTUCTURES FOR WHICH DATA HAVE BEEN INCLUDED. THE

```


1 NUMBERS REFER TO THE ABOVE EQUATIONS.)
 101 FORMAT(1H0)
 102 FORMAT(20X,A2,1H-,A2,4(5X,A3,I5))
 103 FORMAT(20X,A2,3X,4(5X,A3,I5))\$END

SUBROUTINE ALLOY

C READS, CONVERTS AND NORMALIZES COMPOSITION OF AN ALLOY
 COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
 1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
 2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
 3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V
 READ102,TITLE\$PRINT103,TITLE\$READ104,IW,X
 C IF IW = 1 THEN COMPOSITION IS GIVEN IN WEIGHT UNITS
 IF(IW.NE.1)GOTO30\$TA=TB=0.\$DO10I=1,IND\$XA=W(I)=X(I)
 TA=TA+XA\$XA=X(I)=X(I)/AT(I)
 10 TB=TB+XA\$PRINT105\$TA=1./TA\$TB=1./TB\$DO20I=1,IND
 IF(X(I).EQ.0.)GOTO20\$W(I)=W(I)*TA\$X(I)=X(I)*TB
 PRINT106,EL(I),W(I),X(I)
 20 CONTINUE\$RETURN
 30 TA=0.\$DO34I=1,IND
 34 TA=TA+X(I)\$TA=1./TA\$PRINT107\$DO38I=1,IND\$IF(X(I).EQ.0.)GOTO38
 X(I)=X(I)*TA\$PRINT106,EL(I),X(I)
 38 CONTINUE\$RETURN
 102 FORMAT(20A4)
 103 FORMAT(/,10X,20A4,/))
 104 FORMAT(I5,15F5.0)
 105 FORMAT(34H0 WEIGHT % - ATOM % ,/)
 106 FORMAT(2X,A2,2P2F15.3)
 107 FORMAT(22H0 ATOM % ,/) \$END

SUBROUTINE TOTAL

COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
 1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
 2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
 3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V
 PRINT102\$PRINT101,PH\$DO20IT=5,16\$T=IT*100\$DO15K=1,3
 15 GG(K)=GF(K)

```

20 PRINT100,T,(GG(I),I=1,3)$RETURN
100 FORMAT(/,F10.0,5X,4F12.0)
102 FORMAT(20X,22H FREE ENERGY J/MOL ,//)
101 FORMAT(11H0 TEMP, K ,5(9X,A3)/)$END

```

FUNCTION GF(II)

CALCULATES THE FREE ENERGY OF AN ALLOY OR A PURE COMPONENT

```

COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V$COMMON/Z/IQD(676)
KK=K*169-182$TA=0.$DO1N=1,IND$U=X(N)$IF(U.EQ.0.)GOTO1
I=INDEX(M*14+KK)$IF(I.EQ.0)GOTO9
TA=TA+U*(A(I)+T*(B(I)+T*(C(I)+T*(D(I)+T*(E(I))))))
9 TA=TA+U*ALOG(U)*8.3144*T$IF(M.EQ.IND)GOTO1
NN=M+1$DO1N=NN,IND$V=X(N)
IF(V.EQ.0.)GOTO1$I=INDEX(M+N*13+KK)$IF(I.EQ.0)GOTO1
GOTO(10,10,12,13)IC(I)
10 UU=A(I)+B(I)*T$VV=C(I)+D(I)*T$GOTO2
12 UU=A(I)+T*(B(I)+T*(E(I)+T*(F(I)+T*(G(I))))$VV=C(I)+T*(D(I)+T*(E(I)+T*(F(I)+T*(G(I))))$GOTO2
13 UU=A(I)+T*(B(I)+T*(C(I)+T*(D(I))))$VV=E(I)+T*(F(I)+T*(G(I)+T*(H(I))))
2 TA=TA+U*V*(UU+(V-U)*VV)
1 CONTINUE$GF=TA$RETURN$END

```

SUBROUTINE PARTIAL

CALCULATES THE PARTIAL FREE ENERGY OF THE COMPONENTS OF AN ALLOY

```

COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4),PG(13),W(13),X(13),EL(13),PH(5),AT(13),IS(13),TITLE(20)
3,TH(3)/O/NUM,T,IND,K,L,M,N,U,V$DIMENSIONAC(13,10),GT(10),TA(10)
JT=5$PRINT100$DO30K=1,3$PRINT101,PH(K)
DO20IT=1,JT$T=IT*100+1000$T1=0.
DO10L=1,IND$IF(X(L).EQ.0.)GOTO10$XX=AC(L,IT)=PF(K)$T1=T1+XX*X(L)
10 CONTINUE$TA(IT)=T$GT(IT)=T1
20 CONTINUE$PRINT102,(TA(I),I=1,JT)$PRINT101
DO25L=1,IND$IF(X(L).EQ.0.)GOTO25
PRINT103,EL(L),X(L),(AC(L,I),I=1,JT)

```

```

25 CONTINUE$PRINT104, (GT(I), I=1, JT)
30 CONTINUE$RETURN
100 FORMAT (///, 10X, 69H PARTIAL FREE ENERGY/ACTIVITY OF THE ALLOY COM
    1PONENTS OF THE ALLOY ,//)
101 FORMAT (/ , 20X, A3, 8H PHASE ,/)
102 FORMAT (20X, 10F10.0)
103 FORMAT (5X, A2, 3X, F10.3, 10F10.0)
104 FORMAT (6H0 SUM, 14X, 10F10.0) $END

```

```

FUNCTION PF(II)
CALCULATES THE PARTIAL FREE ENERGY OF COMPONENT L.
COMMON/A/A(300)/B/B(300)/C/C(300)/D/D(300)/E/E(300)/F/F(300)
1/G/G(300)/H/H(300)/I/INDEX(676)/L/IC(300)
2/M/GG(4), PG(13), W(13), X(13), EL(13), PH(5), AT(13), IS(13), TITLE(20)
3, TH(3)/O/NUM, T, IND, K, L, M, N, U, V
KK=K*169-182$TA=ALOG(X(L))*8.3144*T$I=INDEX(L*14+KK)
IF(I.NE.0) TA=TA+A(I)+T*(B(I)+T*(C(I)+T*(D(I)+T*(E(I))))
5 DO1M=1, IND$U=X(M)$IF(U.EQ.0..OR.M.EQ.IND) GOTO1$NN=M+1
DO1N=NN, IND$V=X(N)$IF(V.EQ.0.) GOTO1$I=INDEX(M+N*13+KK)
IF(I.EQ.0) GOTO1$GOTO(6,6,7,8) IC(I)
6 UU=A(I)+B(I)*T$VV=C(I)+D(I)*T$GOTO10
7 UU=A(I)+T*(B(I)+T*(E(I)+T*(F(I)+T*(G(I)))) $VV=C(I)+T*(D(I)+T*(E(I)+T*(F(I)+T*(G(I)+T*(H(I))))
8 UU=A(I)+T*(B(I)+T*(C(I)+T*(D(I)))) $VV=B(I)+T*(F(I)+T*(G(I)+T*(H(I))))
10 IF(L.EQ.N) GOTO20$IF(L.EQ.N) GOTO30
TA=TA-U*V*(UU+2.*VV*(V-U)) $GOTO1
20 TA=TA+V*(UU*(1.-U)+VV*(2.*U*(U-1.-V)+V)) $GOTO1
30 TA=TA+U*(UU*(1.-V)+VV*(2.*V*(1+U-V)-U))
1 CONTINUE$PF=TA$RETURN$END

```

```

C ALSITICRMNFECONICUNBHOW LIQBCCFCHCP GHS0302202333222
1201 2698 2809 4790 5200 5494 5585 5893 5871 6354 9291 959418385
ALALLIQG 10711.04 -11.506
ALALBCCG 10083. -4.812
ALALHCPG 5481.04 -1.79912
COCOLIQG 16192.08 -9.16296
CQCOBCCG 6953. -.6353E -2 2.8037E-6
COCOHCPCG -460.24 .6276
CRCRLIQG 18200.4 -8.368

```

CRCRPCCG	10460.	.6276			
CRCRHCPG	8368.				
PEFELIQG	13807.2	-7.6316			
NINILIQG	17614.64	-10.209			
NINIBCCG	3932.96		4.1087	E-3-.4853	E-51.41 E-9
NINIHCPCG	1046.	1.2552			
TITILIQG	16233.92	-8.368			
TITIHCPG	-4351.	3.7656			
TITIFCCG	-1003.8	3.7656			
CRFELIQ	20794.	20794.	10.46	10.46	
CRFEFCC	7405.	7405.	6.276	6.276	
CRFEBCC	25104.	25104.	10.46	10.46	
CRNILIQ	-8368.	-8368.			
CRNIBCC	53555.2	-13388.8	27.196	2.092	
CRNIFCCH3	-8368.	-.4678	E-21.56054E-5	-25104.	-.94772E-25.214 E-6
CRNIFCCS3		-.9374	E-22.34081E-5		-1.8954E-27.82115E-6
FENILIQ	-8368.	-32217.	-2.72	-9.205	
FENIFCCH3	2092.	3.8314E-	3-3.2652E-6	-34881.	-2.4404E-22.0802 E-5
FENIFCCS3		7.6628	E-3-4.899	E-6	-4.8808E-23.1203 E-5
FENIBCCCH3	1339.	-1.3275E-	33.174	E-6-16276.	-3.5412E-22.6382 E-5
FENIBCCS3		-2.655	E-34.761	E-6	-7.0824E-23.9573 E-5
FEFEFCCG	6108.64	-3.4618	-.7472	E-2.5124	E-5
FEFEHCPG	4280.2	1.224	-.7472	E-2.5124	E-5
NBNBLIQG	22928.	-8.368			
NBNBFCCG	8996.	3.556			
NBNBHCPG	6276.	3.347			
MONOLIQG	24267.	-8.368			
MONOPCCG	10460.	.628			
MONOHCPG	8368.				
W W LIQG	30543.	-8.368			
W W FCCG	10460.	.628			
W W HCPG	8368.				
TIFELIQ	-46024.	-62760.			
TIFEBCC	-23012.	-46024.			
TIFEHCP					
TIPEFCC	-10460.	-33472.			
FECOLIQ	-6904.	-12803.	-4.6	-12.38	

FECOBCCCH3	-36945.	-.50034E-14.3401 E-5-39886.	-.43704E-13.3125 E-5
FECOBCCS3		-.10007 6.5102 E-5	-.08741 4.9688 E-5
FECOHCPH3	1443.	-2.0849E-3.85889E- 62782.	-.57333E-22.3621 E-6
FECOHCPH3		-4.1698E-31.288 E-6	-1.1467E-23.5432 E-6
FECOPCCH3	-2322.	-2.0849E-3.85889 E-6-983.	-.57333E-22.3621 E-6
FECOPCCS3		-4.1698E-31.2883 E-6	-1.1467E-23.5432 E-6
FENBLIQ	-15481.	-32217.	
FENBBCC	8786.	16736.	
FENBPCC			
FEMOLIQ		17573.	
FEMOBCC	32217.	33422.	8.368
FEMOPCC	24790.	25376.	8.368
FEW BCC	46861.	50208.	10.878
FEW FCC	42258.	45020.	12.761 1.883
TICRLIQ		12552.	
TICRBCC	12552.	25104.	
TICRHCP	39413.	51966.	
CRCOLIQ	29288.	8368.	41.84
CRCOBCC	29288.	29288.	41.84
CRCOHCP	13807.	-8368.	31.38
CRCOPCC	4602.	-8786.	31.38
CRNBLIQ	5858.	5858.	
CRNBBCC	29288.	22594.	
CRMOLIQ	25522.	12552.	11.3 5.86
CRMOBCC	34309.	21338.	11.3 5.86
CRW LIQ	31380.	28033.	
CRW BCC	31380.	28033.	
TINILIQ	-112968.	-188280.	-29.29 -54.39
TINIBCC	-77822.	-164013.	-29.29 -54.39
TINIHCPC	-44350.	-44350.	-29.29 -29.29
TINIFCC	-90374.	-182422.	-29.29 -54.39
CONILIQ	3347.	3347.	
CONIBCCCH3	27309.	.63417E- 2-1.7358E-527309.	.63417E- 2-1.7358E-5
CONIBCCS3	10.738	1.2683E- 2-2.6037E-510.738	1.2683E- 2-2.6037E-5
CONIHCPH3	3096.	.53815E- 2-5.7396E-63096.	.53815E- 2-5.7396E-6
CONIHCPH3		1.0763E- 2-8.6094E-6	1.0763E- 2-8.6094E-6
CONIFCCH3	4602.	.5381 E-2-5.7396E-64602.	.5315 E-2-5.7396E-6

CONIFCCS3		1.0763E- 2-8.6094E-6		1.0763E- 2-8.6094E-6
NINBLIQ	-154808.	-54392.		
NINBBCC	-25941.	-25941.		
NINBFCC	-148532.	-48116.		
NIMOLIQ	-17573.	-17573.	-13.807	-13.807
NIMOBCC	23430.	23430.	-13.807	-13.807
NIMOFCC	-13598.	-13598.	-13.807	-13.807
NIW LIQ	-31798.	40166.	-20.92	
NIW FCC	-29288.	41840.	-20.92	
TICOLIQ	-142256.	-167360.	-29.29	-54.39
TICOBCC	-109621.	-143093.	-29.29	-54.39
TICOHCP	-64015.	-158992.	29.29	-66.94
TICOFCC	-111294.	-155226.	-29.29	-54.39
NIW BCC	62760.	62760.		
TINBLIQ	13075.	13075.		
TINBBCC	13075.	13075.		
TINBHCP	13075.	13075.		
TIMOLIQ	6527.	6527.		
TIMOBCC	5192.	5192.		
TIMOHCP	15359.	15359.		
TIW LIQ	120970.	6276.	-7.95	
TIW BCC	16318.	16318.	-7.95	
TIW HCP	26359.	26359.	-7.95	
CONBLIQ	-30543.	-13807.		
CONBBCC	32217.	32217.		
CONBHCP	-7113.	-7113.		
CONBFCC	-7113.	-7113.		
COMOLIQ	2510.	2510.		
COMOBCC	29288.	29288.		
COMOHCP	-24539.	-24539.	-21.46	-21.46
COMOFCC	-25104.	-25104.	-20.92	-20.92
COW LIQ	-10878.	-10878.	-10.46	-10.46
COW BCC	56065.	56065.		
COW HCP	4602.	-418.	-10.46	-10.46
COW FCC	-4602.	-4602.	-10.46	-10.46
NNNNLIQG	20878.	-14.7694		
NNNNBCCG	6234.	-5.1464		

MNMNPFCCG	2870.	10.842	-2.124 E-2.8396	E-5
MNMNHCPG	11673.	-7.6564		
CUCULIQG	13054.	-9.623		
CUCUBCCG	6276.	-3.347		
CUCUHCPG	628.	1.255		
TIMNLIQ	-12552.	-12552.		
TIMNBCC				
TIMNHCP	23012.	23012.		
TIMNFCC	-2720.	-2720.		
CRMNLIQ	-12552.	2-12553.	-10.46	-10.46
CRMNBCC	-8786.	-8786.	-10.46	-10.46
CRMNFCC	-17573.	-17573.	-10.46	-10.46
MNFELIQ	-21589.	-19874.	-16.987	-16.987
MNFEBCC	5188.	4100.	-1.506	-4.686
MNFEFCC	-18870.	-18870.	-16.987	-16.987
MNCOLIQ	-30962.	-30962.		
MNCOBCC	-26150.	-26150.		
MNCOHCP	-28660.	-28660.	-2.510	-2.510
MNCOFCC	-23849.	-23849.		
MNNILIQ	-64434.	-76986.	-10.878	-10.878
MNNIBCC	-45606.	-58158.	-3.640	-3.640
MNNIFCC	-51882.	-64434.	-10.878	-10.878
MNCULIQ	-34309.	-24267.	-33.472	-16.736
MNCUBCC	16108.	2929.		
MNCUFCC	18200.	5021.		
TICULIQ	-17573.	-11715.		
TICUBCC	5858.	5858.		
TICUHCP	18410.	18410.		
TICUFCC	4602.	4602.		
COCULIQ	40166.	53555.	8.368	16.736
COCUHCP	29288.	31798.		
COCUFCC	29288.	31798.		
CRCULIQH3	67780.		1032150.	-.83956 2.83276E-4
CRCULIQS3	16.736		1613.6	-1.67912 4.2914E-4
CRCUBCC	104600.	104600.		
CRCUFCC	104600.	104600.		
FECULIQH1	36134.	32508.	7565.	2418.

PECULIQS1	3.50012	.21758	2.58626	2.34777
PECUBCCH2	-33930.	-38070.	.21597	-1.7483E-4.39945 E-7
PECUBCCS2	-217.482	-238.754	.43184	-2.6225E-4.5326 E-7
PECUFCC	54124.	42288.	13.4637	3.4292
NICULIQ	10021.	858.	-1.4644	-5.732
NICUFCC	11632.	2469.	.2092	-4.058
CUNBLIQ	111294.	111294.	41.84	41.84
CUNBBCC	46024.	46024.		
CUNBFCC	98742.	98742.	41.84	41.84
C C LIQG	114223.	-27.196		
C C BCCG	81588.	-14.646		
C C FCCG	73222.	-14.646		
C C HCPG	48953.	-14.646		
C ALLIQ	-78659.	9623.		
C TILIQ	-175728.	-175728.		
C TIBCC	-209200.	-209200.		
C CRLIQ	-138072.	-138072.		
C CRBCC	-133888.	-133888.		
C MNLIQ	-166523.	-99579.	-47.968	4.602
C MNBCC	-269031.	-118407.	-47.698	4.602
C MNHCP	-25344.	-169034.	-79.496	-16.736
C MNFCC	-288278.	-141419.	-47.698	4.602
C FELIQ	-156063.	-91630.	-48.953	-10.544
C FEBCC	-95814.	-35146.	29.079	37.823
C FEPCC	-155226.	-94558.	-5.816	2.929
C COLIQ	-94558.	-94558.	-25.1	-25.1
C COHCP	-95814.	-59831.	-6.02	11.0
C COPCC	-95814.	-59831.	-6.02	11.
C NILIQ	-99579.	-111294.	-15.36	-42.97
C NIFCC	-108784.	-79496.	-67.7	-4.31
C NBLIQ	-110458.	-110458.	20.92	20.92
C NBBCC	-169034.	-169034.	20.92	20.92
C HOLIQ	-129704.	-71128.		
C HOBCC	-37656.	-37656.		
C W LIQ	-83680.	-37656.		
C W BCC	16736.	16736.		
ALTILIQ	-100834.	-100834.	-41.84	-41.84

ALTIBCC	-117152.	-117152.	-41.84	-41.84		
ALTIHCP	-121336.	-121336.	-41.84	-41.84		
ALTIFCC	-101253.	-101253.	-41.84	-41.84		
ALCRLIQ	-46442.	-46442.				
ALCRBCC	-60250.	-60250.				
ALMNLIQ	-57321.	-57321.	-22.761	-22.761		
ALMNBCC	-73220.	-73220.	-22.761	-22.761		
ALMNFCC	-48116.	-69036.	-22.761	-22.761		
ALFELIQ	-96232.	-62760.	-33.054	4.602		
ALFEBCC	-175728.	-58576.	-71.128	14.226		
ALFEFCC	-112968.	-51296.	-71.128	14.266		
ALCOLIQH3	-455638.	.1854	-2.3756E-4	-107110.	.11316	-.61171E-4
ALCOLIQS3	-117.624	.37079	-3.5634E-4	-118.382	.22632	-.91755E-4
ALCOBCCCH3	-450617.	.1854	-2.3756E-4	-93303.	.11316	-.61171E-4
ALCOBCCS3	-92.521	.3709	-3.5634E-4	-100.684	.22632	-.91755E-4
ALCOHCAPH3	-102090.			-164850.	.3609	-2.653 E-4
ALCOHCPS3				-266.868	.7218	-3.9844E-4
ALCOFCCCH3	-104600.			-167360.	.3609	-2.6563E-4
ALCOFCCS3				-266.868	.7218	-3.9844E-4
ALNLIQH3	-92081.	-1.3924E-15	.4626E-5	-203376.	-1.3924E-15	.4626E-5
ALNLIQS3	130.206	-27.848E-281	.939E-6	6138.15	-27.848E-281	.939E-6
ALNIFCCH3	-19907.	-1.3924E-15	.4626E-5	-189987.	-1.3924E-15	.4626E-5
ALNIFCCS3	182.506	-27.848E-281	.939E-6	6149.452	-27.848E-281	.939E-6
ALNIBCCCH3	-281662.	.92048E-1	-3.6116E-5	-220984.	-1.3924E-15	.4626E-5
ALNIBCCS3	-220.622	18.410E-2	-54.174E-6	6141.084	-27.848E-281	.939E-6
ALCULIQ	-25104.	-41840.	5.858	23.849		
ALCUBCC	103127.	-162419.	106.483	-51.882		
ALCUFCC	-6736.	-84098.	.711	-1.841		
ALNB LIQ	-209200.	-209200.	-67.781	-67.781		
ALNBBCC	-213384.	-213384.	-67.781	-67.781		
ALMOLIQ	-46024.	-46024.				
ALMOBCC	-16736.	-30543.	12.552			
ALW LIQ	-33472.	-33472.	-26.15	-26.15		
ALW BCC	-23849.	-23849.	-26.15	-26.15		
SISILIQG	50626.	-30.				
SISIBCCG	44350.	-19.54				
SISIFCCG	50626.	-17.87				

SISIHCPG	50208.	-17.87		
C SILIQ	35564.	35564.	5.439	5.439
ALSILIQ	19916.	29121.	41.17	41.17
ALSIFCC	25773.	34978.	41.17	41.17
SITILIQ	-132214.	-182422.	37.66	37.66
SITIBCC	-210874.	-169034.	25.10	25.10
SITIHCP	-287859.	-246019.	-43.52	-43.52
SICRLIQ	-112968.	-87864.	-33.472	33.472
SICRBCC	-106692.	-81588.	-29.288	37.656
SIMNLIQ	-81170.	-101253.	-2.092	23.012
SIMNBCC	-72802.	-92885.	-2.092	23.012
SIMNFCC	-84098.	-104184.	-2.092	23.012
SIFELIQ	-108366.	-173636.	-17.57	-38.49
SIFEBCC	-297064.	-129704.	-136.82	-7.95
SIFEPC	-304177.	-136817.	-136.82	-7.95
SICOLIQ	-135980.	-204179.	-32.01	-32.01
SICOPCC	-141419.	-209618.	-32.01	-32.01
SICOHCP	-142256.	-210455.	-32.01	-32.01
SINILIQ	-133888.	-259994.	-22.01	-62.01
SINIFCC	-138239.	-264345.	-22.01	-62.01
SICULIQ	137654.	-231375.	96.232	-96.232
SICUFCC	138365.	-230245.	96.232	-96.322
SICUBCC	179075.	-199158.	96.232	-96.232
SINBLIQ	-175728.	-234304.	37.238	-41.84
SINBBCC	-280238.	-115063.		
SIMOLIQ	-83680.	-83680.		
SIMOBCC	-61923.	-61923.		
SIW LIQ	-29288.	-29288.		
SIW BCC	-15899.	-15899.		
FEW LIQ	19748.	20920.	5.44	-5.44

9

UNITEMP AF 1753

4-9-81

1

1.1

0.9 19.6

11.2 8.8 48.4

1.7 8.3

ELEMENT AT WEIGHT STD STATE

1	C	12.01	
2	AL	26.98	FCC
3	SI	28.09	
4	TI	47.90	BCC
5	CR	52.00	BCC
6	MN	54.94	
7	FE	55.85	BCC
8	CO	58.93	FCC
9	NI	58.71	FCC
10	CU	63.54	FCC
11	NB	92.91	BCC
12	MO	95.94	BCC
13	W	183.85	BCC

LISTING OF THE FREE ENERGY EXPRESSIONS

1	LIQ	AL	G =	10711. +	-11.51*T			
2	BCC	AL	G =	10083. +	-4.81*T			
3	HCP	AL	G =	5481. +	-1.80*T			
4	LIQ	CC	G =	16192. +	-9.16*T			
5	BCC	CO	G =	6953. +	0.0 *T	+ -.6353E-02*T**2	+ 0.2804E-05*T**3	
6	HCP	CO	G =	-460. +	0.63*T			
7	LIQ	CR	G =	18200. +	-8.37*T			
8	FCC	CR	G =	10460. +	0.63*T			
9	HCP	CR	G =	8368. +	0.0 *T			
10	LIQ	FE	G =	13807. +	-7.63*T			
11	LIQ	NI	G =	17615. +	-10.21*T			
12	BCC	NI	G =	3933. +	0.0 *T	+ 0.4109E-02*T**2	+ -.4853E-05*T**3	+ 0.1410E-08*T**4
13	HCP	NI	G =	1046. +	1.26*T			
14	LIQ	TI	G =	16234. +	-8.37*T			
15	HCP	TI	G =	-4351. +	3.77*T			
16	FCC	TI	G =	-1004. +	3.77*T			
17	LIQ	G = CRFE(	CR(	20794. +	-10.46*T)	+ FE(	20794. +	-10.46*T)
18	FCC	G = CRFE(	CR(	7405. +	-6.28*T)	+ FE(	7405. +	-6.28*T)
19	BCC	G = CRFE(	CR(	25104. +	-10.46*T)	+ FE(	25104. +	-10.46*T)
20	LIQ	G = CRNI(	CR(	-8368. +	0.0 *T)	+ NI(	-8368. +	0.0 *T)
21	BCC	G = CRNI(	CR(	53555. +	-27.20*T)	+ NI(	-13389. +	-2.09*T)
22	FCC	G = CRNI(	CR(	-8368.+	0.0 *T+0.4687E-02*T**2+-.7803E-05*T**3)	+NI(	-25104.+	0.0 *T+0.9477E-02*T**2+-.2607E-05*T**3))
23	LIQ	G = FENI(	FE(	-8368. +	2.72*T)	+ NI(	-32217. +	9.20*T)
24	FCC	G = FENI(	FE(	2092.+	0.0 *T+-.3831E-02*T**2+0.1633E-05*T**3)	+NI(	-34881.+	0.0 *T+0.2440E-01*T**2+-.1040E-04*T**3))
25	BCC	G = FENI(	FE(	1339.+	0.0 *T+0.1327E-02*T**2+-.1587E-05*T**3)	+NI(	-16276.+	0.0 *T+0.3541E-01*T**2+-.1319E-04*T**3))

26	FCC	FE	G =	6109. +	-3.46*T	+ -.7472E-02*T**2	+ 0.5124E-05*T**3
27	HCP	FE	G =	4280. +	1.22*T	+ -.7472E-02*T**2	+ 0.5124E-05*T**3
28	LIQ	NB	G =	22928. +	-8.37*T		
29	FCC	NB	G =	8996. +	3.56*T		
30	HCP	NB	G =	6276. +	3.35*T		

STRUCTURES FOR WHICH DATA HAVE BEEN INCLUDED. THE NUMBERS REFER TO THE ABOVE EQUATIONS.

C	LIQ	153	BCC	154	FCC	155	HCP	156
C -AL	LIQ	157						
C -SI	LIQ	212						
C -TI	LIQ	158	BCC	159				
C -CR	LIQ	160	BCC	161				
C -MN	LIQ	162	BCC	163	FCC	165	HCP	164
C -PE	LIQ	166	BCC	167	FCC	168		
C -CO	LIQ	169	FCC	171	HCP	170		
C -NI	LIQ	172	FCC	173				
C -CU								
C -NB	LIQ	174	BCC	175				
C -MO	LIQ	176	BCC	177				
C -W	LIQ	178	BCC	179				

AL-C	LIQ	157						
AL	LIQ	1	BCC	2	HCP	3		
AL-SI	LIQ	213	FCC	214				
AL-TI	LIQ	180	BCC	181	FCC	183	HCP	182
AL-CR	LIQ	184	BCC	185				
AL-MN	LIQ	186	BCC	187	FCC	188		
AL-PE	LIQ	189	BCC	190	FCC	191		
AL-CO	LIQ	192	BCC	193	FCC	195	HCP	194
AL-NI	LIQ	196	BCC	198	FCC	197		
AL-CU	LIQ	199	BCC	200	FCC	201		
AL-NB	LIQ	202	BCC	203				
AL-MO	LIQ	204	BCC	205				
AL-W	LIQ	206	BCC	207				

SI-C	LIQ	212						
SI-AL	LIQ	213	FCC	214				
SI	LIQ	208	BCC	209	FCC	210	HCP	211
SI-TI	LIQ	215	BCC	216	HCP	217		
SI-CR	LIQ	218	BCC	219				
SI-MN	LIQ	220	BCC	221	FCC	222		
SI-PE	LIQ	223	BCC	224	FCC	225		
SI-CO	LIQ	226	FCC	227	HCP	228		
SI-NI	LIQ	229	FCC	230				
SI-CU	LIQ	231	BCC	233	FCC	232		
SI-NB	LIQ	234	BCC	235				
SI-MO	LIQ	236	BCC	237				
SI-W	LIQ	238	BCC	239				

TI-C	LIQ	158	BCC	159		
TI-AL	LIQ	180	BCC	181	FCC	183
TI-SI	LIQ	215	BCC	216	HCP	217
TI	LIQ	14	FCC	16	HCP	15
TI-CR	LIQ	53	BCC	54	HCP	55
TI-MN	LIQ	115	BCC	116	FCC	118
TI-Fe	LIQ	37	BCC	38	FCC	40
TI-CO	LIQ	82	BCC	83	FCC	85
TI-NI	LIQ	66	BCC	67	FCC	69
TI-CU	LIQ	135	BCC	136	FCC	138
TI-NB	LIQ	87	BCC	88	HCP	89
TI-MO	LIQ	90	BCC	91	HCP	92
TI-W	LIQ	93	BCC	94	HCP	95

W LIQ 34 FCC 35 HCP 36

UNITED STATES OF AMERICA 4-9-81

WEIGHT % - ATOM %

AL	1.100	2.436
TI	0.900	1.123
CR	19.600	22.522
FE	11.200	11.982
CC	8.800	8.923
NI	48.400	49.258
BC	1.700	1.059
W	8.300	2.697

FREE ENERGY J/MOL

TEMP. K	LIQ	BCC	FCC	HCP
500.	878.	-4572.	-9429.	
600.	-1217.	-5793.	-10609.	
700.	-3292.	-7000.	-11762.	
800.	-5347.	-8199.	-12890.	
900.	-7383.	-9392.	-13996.	
1000.	-9401.	-10580.	-15081.	
1100.	-11403.	-11763.	-16147.	

1200.	-13389.	-12939.	-17197.
1300.	-15360.	-14103.	-18232.
1400.	-17317.	-15251.	-19254.
1500.	-19262.	-16374.	-20266.
1600.	-21196.	-17465.	-21269.

PARTIAL FREE ENERGY/ACTIVITY OF THE ALLOY COMPONENTS OF THE ALLOY

LIQ PHASE		1100.	1200.	1300.	1400.	1500.
AL	0.024	-162895.	-162675.	-161862.	-160496.	-158618.
TI	0.011	-99028.	-100905.	-102796.	-104701.	-106617.
CR	0.225	-2414.	-5032.	-7665.	-10311.	-12969.
FE	0.120	-15294.	-17783.	-20286.	-22802.	-25331.
CO	0.089	-15611.	-18861.	-22077.	-25246.	-28359.
NI	0.493	-5137.	-6483.	-7824.	-9162.	-10501.
MO	0.011	-19158.	-23455.	-27765.	-32089.	-36425.
W	0.027	6654.	3559.	450.	-2673.	-5807.
SUM		-11403.	-13389.	-15360.	-17317.	-19262.

BCC PHASE		1100.	1200.	1300.	1400.	1500.
AL	0.024	-177322.	-176636.	-175546.	-174054.	-172158.
TI	0.011	-90657.	-91735.	-92831.	-93940.	-95060.
CR	0.225	-8705.	-11219.	-13752.	-16298.	-18854.
FE	0.120	-12953.	-14002.	-15200.	-16579.	-18174.
CO	0.089	-11605.	-13675.	-15445.	-16873.	-17916.
NI	0.493	-4517.	-4881.	-5250.	-5616.	-5965.
MO	0.011	-10899.	-14467.	-18053.	-21652.	-25261.
W	0.027	17143.	13946.	10734.	7507.	4270.
SUM		-11763.	-12939.	-14103.	-15251.	-16374.

FCC PHASE		1100.	1200.	1300.	1400.	1500.
-----------	--	-------	-------	-------	-------	-------

AL	0.024	-135812.	-136307.	-136283.	-135776.	-134825.
TI	0.011	-94981.	-95713.	-96437.	-97147.	-97838.
CR	0.225	-5105.	-6940.	-8878.	-10926.	-13095.
FE	0.120	-18672.	-20336.	-21845.	-23179.	-24319.
CO	0.089	-22299.	-24816.	-27241.	-29550.	-31716.
NI	0.493	-12178.	-12369.	-12564.	-12771.	-12999.
MO	0.011	-20590.	-23707.	-26817.	-29912.	-32988.
W	0.027	-6646.	-9055.	-11456.	-13843.	-16211.
SUM		-16147.	-17197.	-18232.	-19254.	-20266.

ORNL-5781
Distribution
Category UC-90h

INTERNAL DISTRIBUTION

1-2. Central Research Library	27. T. W. Pickel
3. Document Reference Section	28. H. E. Reesor
4-5. Laboratory Records Department	29. P. L. Rittenhouse
6. Laboratory Records, ORNL RC	30. J. H. Schneibel
7. ORNL Patent Section	31. S. Y. Shiao
8. V. B. Baylor	32. V. K. Sikka
9. R. A. Bradley	33. G. M. Slaughter
10. C. R. Brinkman	34. J. O. Stiegler
11. R. E. Clausing	35. R. W. Swindeman
12. D. P. Edmonds	36. T. N. Tiegs
13. J. P. Hammond	37. P. F. Tortorelli
14. R. L. Heestand	38. R. Triolo
15-17. M. R. Hill	39. C. L. White
18. J. K. Huffstetler	40-44. R. O. Williams
19. J. E. Jones, Jr.	45. M. H. Yoo
20. R. R. Judkins	46. A. L. Bement, Jr. (Consultant)
21. E. A. Kenik	47. E. H. Kottcamp, Jr., (Consultant)
22. D. L. Lennon	48. Alan Lawley (Consultant)
23. M. B. Lewis	49. T. B. Massalski (Consultant)
24. Jar-Shyong Lin	50. R. H. Redwine (Consultant)
25. P. J. Maziasz	51. A. D. Rossin (Consultant)
26. R. K. Nanstad	

EXTERNAL DISTRIBUTION

- 52-53. DOE, OFFICE OF FOSSIL ENERGY, 20 Massachusetts Avenue N. W.,
Washington, DC 20545

S. J. Dapkunas
John Fairbanks

54. DOE, Oak Ridge Operations Office, P.O. Box E, Oak Ridge, TN 37830

Office of Assistant Manager for Energy Research and Development

- 55-282. DOE, TECHNICAL INFORMATION CENTER, OFFICE OF INFORMATION SERVICES,
P.O. Box 62, Oak Ridge, TN 37830

For distribution as shown in TID-4500 Distribution Category,
UC-90h (Coal Conversion and Utilization - (Materials and
Components).