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THIRD-ELEMENT INTERACTIONS WITH THE SYSTEM LIQUID IRON - LIQUID CALCIUM

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PREFACE

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ABSTRACT

The purpose of this investigation was to determine the solubility of calcium in liquid iron and the effects of various third elements upon the solubility. These relationships have not been investigated previously because of the considerable experimental problems in attaining equilibrium between liquid calcium and liquid iron at temperatures in the range of 2925°F.

By using a chamber pressurized with argon and containing an induction furnace, the desired melts were made in specially developed titanium nitride crucibles and samples were taken by remote controls. The data indicate that liquid calcium and liquid iron are immiscible and, at 2925°F., the solubility of calcium in iron is 0.032 wt%. Of the third elements tested, carbon is most effective in increasing the solubility of calcium, followed in order by silicon, aluminum and nickel. Gold decreases the solubility. The calcium-iron-carbon-system contains an interesting inflection point; when the carbon content reaches a value of about 0.87 wt%, the CaC_2 phase replaces the metallic calcium and the calcium concentration in the iron decreases. The maximum solubility 0.36 wt% calcium, was obtained in an alloy containing 10.5 wt% silicon in the iron.

The data have interesting applications both in process metallurgy and in providing material for testing the theories of metallic solutions of Alcock and Richardson and of C. Wagner. In the engineering field a variety of calcium-bearing ferroalloys have been used in steelmaking without any basic knowledge of the solubility of calcium. The data of this report should lead to more effective calcium alloy design and use in deoxidizing and other refining reactions. Furthermore the development of the processing procedure

for the new titanium nitride crucibles and the design of the remotely controlled melt sampler should permit the exploration of many interesting but reactive alloy systems which could not be investigated to the present time.

The application of the data to theories of third-element effects in systems of restricted solubility is rewarding. Reasonably good agreement is found with current theories, and criteria are suggested which permit these theories to be applied more readily to systems of this type.

INTRODUCTION

The nature and behavior of liquid metals have eluded the complete understanding of metallurgists and other investigators even to the present day. This is largely due to the difficulty of examining structures in liquid metals, and to the relatively high melting points of most metals of engineering interest.

One very important aspect of liquid-metal behavior is the relative ease with which an element can dissolve in a liquid metal. Unlike the case of solid solubility, which can be estimated rather well by use of the Hume-Rothery rules, relatively little is known about the factors influencing solubility in liquid metals.(1) Such information is highly desired, however, in connection with such engineering problems as the control of impurity levels in liquid metals, the use of magnesium in nodular iron production, the use of liquid metal alloys as nuclear fuels, and as coolants in nuclear power plants and other heat transfer applications. From a theoretical point of view such information should be helpful in advancing the understanding of the structure of liquid metals.

One important example of restricted solubility concerns the extent to which calcium will dissolve in liquid iron. This is a matter of considerable importance in view of the strong potential of calcium for removing certain impurities in steel, as well as the ability of calcium to desulfurize, inoculate, and produce spheroidal graphite in cast irons.(2) Since most ferrous alloys contain other elements, it is important to investigate the interactions of third elements with the calcium-iron system.

A. Purpose of the Investigation

In view of these considerations, the purpose of this study was to investigate the effects of third elements upon the solubility of calcium in liquid iron. For reasons of theoretical and engineering importance, the elements investigated were aluminum, carbon, gold, nickel, and silicon.

REVIEW OF THE LITERATURE

For convenience, the literature pertinent to this investigation may be considered under two categories:

A. Experimental studies.

B. Theoretical considerations.

A. Experimental Studies

Several attempts to determine the solubility of calcium in liquid iron were conducted during the early part of the present century. None of these investigations, however, established the solubility of calcium in liquid iron with any degree of certainty.

Quasebart attempted in 1906 to dissolve calcium in open steel melts by several techniques, with negative results.(3) In the same year, Watts reacted excess calcium with powdered iron oxide in an exothermic reaction within a simple pressure vessel.(4) A piece of the melt was found to contain 0.3% calcium, which Watts considered to be mechanically entrapped, in view of the vigorous nature of the reaction. In 1908 Hirsch and Aston reported negative results for their attempts to alloy iron with calcium in three types of open-melt experiments.(5) In an exothermic bomb-type reaction similar to that of Watts, they obtained pieces of iron analyzing from 0.29% calcium to 1.37% calcium, and considered that at least some of the calcium was alloyed with the iron.

Later writers considered that any calcium reported in the investigations just described was mechanically entrapped in the liquid, with Wever considering calcium as well as the other alkaline earth and the alkali metals categorically to be insoluble in liquid and solid iron.(6,7)

All these investigations were unsatisfactory in that they failed to insure the pressure of a calcium liquid layer in contact with the liquid iron. In the open-melt studies the calcium would have boiled off immediately, and in the bomb-type studies, the calcium presumably would have distilled off to the much colder walls of the container. Furthermore, it was not possible to draw samples directly from the liquid iron in the bomb-type experiments. Any calcium that might have dissolved in the liquid iron could have been rejected by the solid iron during solidification.

These early investigations are of considerable value, however, because they indicate at least that liquid calcium and liquid iron are immiscible. This follows from a consideration of the vapor pressure of calcium, which is approximately 30 psi at the melting point of iron, 2802°F.(8) If iron and calcium formed ideal solutions, then the vapor pressure of calcium would not reach the boiling point, 14.7 psi, until the calcium level reached approximately 50 at%. In this case it might be expected that up to 50 at% calcium could be dissolved in liquid iron just above its melting point in an open melt. Even if strong positive deviations from Raoult's law existed in this system, a calcium solubility of at least 5 to 10 at% might still be expected. Since no calcium was detected in the open melt studies, a miscibility gap is indicated for the iron-calcium system. This observation is consistent with the criterion for immiscibility first formulated by Hildebrand and Scott, and also with the adaptation of this criterion for metals by Mott, from which an immiscibility between iron and calcium is clearly predicted.(9,10)

Little work has been done to measure the solubility of calcium in liquid iron since the time of the investigations described above, presumably because of the severe experimental difficulties involved. In recent years Philbrook and co-workers used radioactive calcium in a study intended to take advantage of the minute concentrations of this species which can be detected.(11) In this study, the calcium was present as CaO in a slag layer, and it was hoped that a sufficient amount of the radioactive calcium would dissolve to permit detection. No calcium was detected in the iron melt, however, even after equilibration at the highest temperature studied, 1800°C (3272°F). Thermodynamic calculations would indicate that if metallic calcium is used instead of CaO at this temperature, then the order-of-magnitude upper limit for calcium solubility in pure iron would be 0.1 wt%.

Recently, Trojan and Flinn have reported magnesium solubilities as high as 3 wt% in liquid iron containing carbon and silicon in the presence of a magnesium-rich layer.(12) Traditionally magnesium, like calcium, had been considered insoluble in liquid iron. Considering the Goldschmidt atomic radii,

Fe(BCC)	1.28 Angstrom units
Mg	1.60 Angstrom units
Ca(FCC)	1.97 Angstrom units

calcium would be expected to be considerably less soluble than magnesium in liquid iron.(13) Nevertheless, significant levels of calcium solubility in liquid iron and iron-base alloys might reasonably be expected on the basis of the rather high solubility of magnesium.

B. Theoretical Considerations

Two theoretical models are of particular interest in relation to the effects of third elements upon the activity or upon the solubility of one element in another. The models, which are due to Alcock and Richardson and to Wagner, are considered in this section.

1. Chemical Model.

Alcock and Richardson have considered the energies involved in breaking old bonds and creating new ones when solute 2 is added to a dilute solution of solute 3 in solvent 1.(14) Assuming no clustering of atoms, and that all atoms have the same coordination number, they obtain the relationship:

$$\left(\frac{\partial \ln \gamma_{2(1,3)}}{\partial N_3}\right)_{N_3 \rightarrow 0} = \epsilon_2^3 = \ln \gamma_{2(3)} - \ln \gamma_{2(1)} - \ln \gamma_{3(1)}, \qquad (1)$$

where

$\gamma_{A(B)}$ = activity coefficient of A in B,

N_A = mole fraction of A

ϵ = interaction parameter.

This equation relates the interaction parameter to activity coefficients in the three binary alloys, and would permit the prediction of the effect which a third element would have upon the activity (and upon the solubility when the activity of solute 2 is relatively constant) of solute 2 for situations where the appropriate activity data are available.

2. Electron Model

Wagner has proposed a theory of considerable interest concerning dilute ternary alloys.(15) This theory states that the activity of a solute metal 2 will be increased by a third component if metals 2 and 3 change the electron-to-atom ratio in the same direction. Conversely, the activity of a solute metal 2 will be decreased by a third component if metals 2 and 3 change the electron-to-atom ratios in opposite directions.

This theory assumes that metal 2 is at least partially dissociated into positive ions and electrons, and that interactions between positive ions are unimportant. The physical basis for this theory is that the chemical potential of electrons in the solvent metal is raised by the addition of solute atoms having a greater number of free electrons than the solvent atoms, and is lowered by the addition of solute atoms having a smaller number of free electrons than that possessed by the solvent. Here the chemical potential is considered to increase as the Fermi energy of the electrons increases. The solubility of solute atom 2 in a solvent 1 should therefore be enhanced under conditions of relatively constant activity of 2 by the addition of solute atom 3 when 2 and 3 tend to change the electron-to-atom ratio of the alloy in opposite directions because this combination changes the chemical potential of the electrons less than if 2 were added alone.

Furthermore, Wagner derives the following equation for the electron-to-atom-ratio concept:

$$\epsilon_2^3 = \epsilon_3^2 = \pm [\epsilon_2^2 \epsilon_3^3]^{1/2}_{N_2 \to 0,\ N_3 \to 0}, \tag{2}$$

where

$$\epsilon_2^3, \text{ etc.} = \frac{\partial \ln \gamma_2}{\partial N_3}, \text{ etc.}$$

2 and 3 = solute atoms

γ = activity coefficient of a species in the solvent

N = mole fraction of a species in the solvent

In this equation the terms ϵ_2^2 and ϵ_3^3 represent self-interaction parameters for the binaries 1-2 and 1-3, respectively. These parameters are a measure of the change in activity coefficient of the solute with changing solute concentration, and are therefore related to deviations from ideality in the binary system.

Equation (2) permits the interactions between two solute atoms to be predicted from a knowledge of activity in the respective binaries of the solutes with the solvent. This equation agrees well with experimental data reported by Wagner for three ternary amalgams. However, use of the equation suffers from the limitations that very few values of self-interaction parameters are available, that self-interaction parameters having opposite signs result in imaginary values of interaction parameters, and that the sign of the interaction parameter must be determined by qualitative considerations. Nevertheless, Equation (2) is of sufficient interest to warrant consideration in this investigation.

EXPERIMENTAL METHOD

In this investigation calcium solubility is measured in liquid-iron melts which contain nominally 0, 2, 5, 10 and 20 at% alloying element. (In the carbon series, studies are at 2, 5, and 10 at% carbon.) Experimental melts are made under argon pressure, in order to prevent boiling away of the calcium, a technique used by Trojan and Flinn to study equilibria between magnesium-base liquids and iron-base liquids.(12)

In this section equilibria between phases in such a pressurized system are analyzed by use of the Phase Rule of J. W. Gibbs. In addition, the more important aspects of the experimental technique are described.

A. Phase-Rule Analysis

The phase rule is a powerful tool in controlling and understanding equilibria between two or more phases. It may be written

$$V = C + 2 - P, \tag{3}$$

where

V = variance of the system,

C = the number of components,

P = the number of phases present.(16)

Here the "2" represents the phase-rule variables temperature and total pressure of the system. The significance of the variance, which is sometimes referred to as the number of "degrees of freedom", is that it specifies how many of the phase-rule variables of temperature, pressure and composition must have values assigned to them in order that the remaining phase-rule variables are uniquely specified. The phase-rule can be applied first to the liquid iron-liquid calcium system under argon pressure, and then to the liquid iron-liquid calcium system to which an alloying element has been added, again under pressure of argon.

1. Iron-Calcium System Under Argon Pressure

When liquid iron is equilibrated with liquid calcium in the presence of argon, the terms in the phase-rule equation (3) become:

$$C = 3 \text{(iron, calcium, argon)}$$

$$P = 3 \text{(iron-rich liquid, calcium-rich liquid, gas)}$$

Hence the variance becomes

$$V = 2.$$

However, both temperature and pressure are held constant (2925°F, 200 psig, respectively) in this investigation; therefore

$$V = 0.$$

This means that the equilibrium compositions of all three phases are fixed for the given temperature and pressure in question and the solubility of calcium in iron should be a unique value.

2. Iron-Calcium-Alloying Element X System Under Argon Pressure

When an alloying element X is added to the above system, the number of components increases to four, and the variance at a fixed temperature and pressure in the presence of the same three phases therefore becomes:

$$V = 1.$$

From this it is seen that by fixing one of the composition variables in the system at equilibrium, the values of all the remaining composition variables can be uniquely specified. Thus the remaining composition variables can be plotted as unique functions of one of the composition variables. Since the number of dimensions required to graphically portray an equilibrium is V + 1, a two-dimensional plot results.(16) If $N_X^{Fe(L)}$, the concentration of the alloying element X in the iron-rich liquid, is plotted as the abscissa, then all the remaining compositional variables can be plotted as ordinates against $N_X^{Fe(L)}$, resulting in a set of unique curves. These remaining variables are

$N_X^{Ca(L)}$, N_X^G = concentrations of alloying element X in the calcium-rich liquid and gaseous phase, respectively.

$N_{Ca}^{Fe(L)}$, $N_{Ca}^{Ca(L)}$, N_{Ca}^G = concentrations of calcium in the iron-rich liquid, calcium-rich liquid and gaseous phase, respectively.

$N_{Fe}^{Fe(L)}$, $N_{Fe}^{Ca(L)}$, N_{Fe}^G = concentrations of iron in the iron-rich liquid, the calcium-rich liquid and gaseous phase, respectively.

$N_A^{Fe(L)}$, $N_A^{Ca(L)}$, N_A^G = concentrations of argon in the iron-rich liquid, calcium-rich liquid and gaseous phase, respectively.

Of the compositional variables presented here, the one of particular interest in this investigation is $N_{Ca}^{Fe(L)}$, the concentration of the calcium in the iron-rich liquid. The values of N_X^G and N_{Fe}^G are quite small because of the low vapor pressures of the present elements and of iron, respectively.

3. Effect of Argon Pressure Upon Equilibrium

The inert gas argon is provided at a pressure above the vapor pressure of the calcium, to prevent boiling away of the calcium. The manner in which the argon enters into equilibrium with the system is of considerable interest.

Argon does not have measurable solubility in liquid metals.(17) The terms $N_A^{Fe(L)}$ and $N_A^{Ca(L)}$ in the previous section become therefore essentially zero. The term N_A^G is not zero, and increases as the externally applied argon pressure increases, since it represents the concentration of the argon in the gaseous phase.

Now the concentration of argon remains unchanged (essentially zero) in the two liquid layers as the argon pressure in the system is increased. Thus, the equilibrium between the liquid layers is not affected by a change in the amount of dissolved argon. Furthermore, the effect of a change in pressure itself upon the equilibrium between two liquid phases at constant temperature is expected to be quite small, by virtue of the thermodynamic relationship

$$\left(\frac{\partial \Delta F}{\partial P} \right)_T = \Delta V, \tag{4}$$

where ΔF = the change in free energy associated with the equilibration of the two liquid layers

ΔV = the volume change associated with the equilibration of the two liquid layers

P = pressure

T = temperature.(18)

Since the volume change ΔV involved in having calcium and iron dissolve slightly in each other is expected to be quite small, the pressure dependence of the free energy change ΔF of the process should also be quite small, indicating a negligible effect of pressure upon solubility.

The above considerations have been borne out experimentally by Trojan and Flinn, who found the solubility of liquid magnesium in liquid iron-carbon alloys was unaffected when the argon pressure of the system was varied by a factor of four.(12) Therefore, as long as the externally applied argon pressure is sufficient to maintain a calcium-rich liquid layer, the compositions of the two liquid layers are relatively independent of the pressure of the system. Specifying the pressure serves only to permit the composition of the gaseous phase to be specified. In situations where this is not of interest, pressure need not be considered as a phase rule variable. The present investigation is just such a case. Pressure is held constant throughout the study for experimental purposes, but the same results are to be expected at any pressure sufficient to maintain a calcium-rich layer.

B. Pressure Chamber

The experimental pressure chamber used by Trojan and Flinn is employed in this investigation and is shown in Figure 1. This consists of a heavy-walled pressure vessel made of austenitic stainless steel, an associated system for controlling pressure and other control devices. The interior of the pressure shell and the port for the power leads are water-cooled to avoid heating by the 3000 cycle induction heating power supply. It was necessary to redesign the interior furnace components to carry out this investigation. The new features of design are described in subsequent sections.

C. Arrangement for Sampling in Place

In developing the experimental phase of this investigation, it seemed highly desirable to develop a method which would permit sampling of the iron-base melt *in situ*. The essential components of the experimental apparatus for accomplishing this are shown schematically in Figure 2, and are considered in detail in the following sections.

1. Coil Assembly

The crucible is contained within an inner graphite vapor lock, the purpose of which is to retard the loss of calcium by gaseous diffusion. A hole is provided in the upper half of this vapor lock. At the time of sampling,

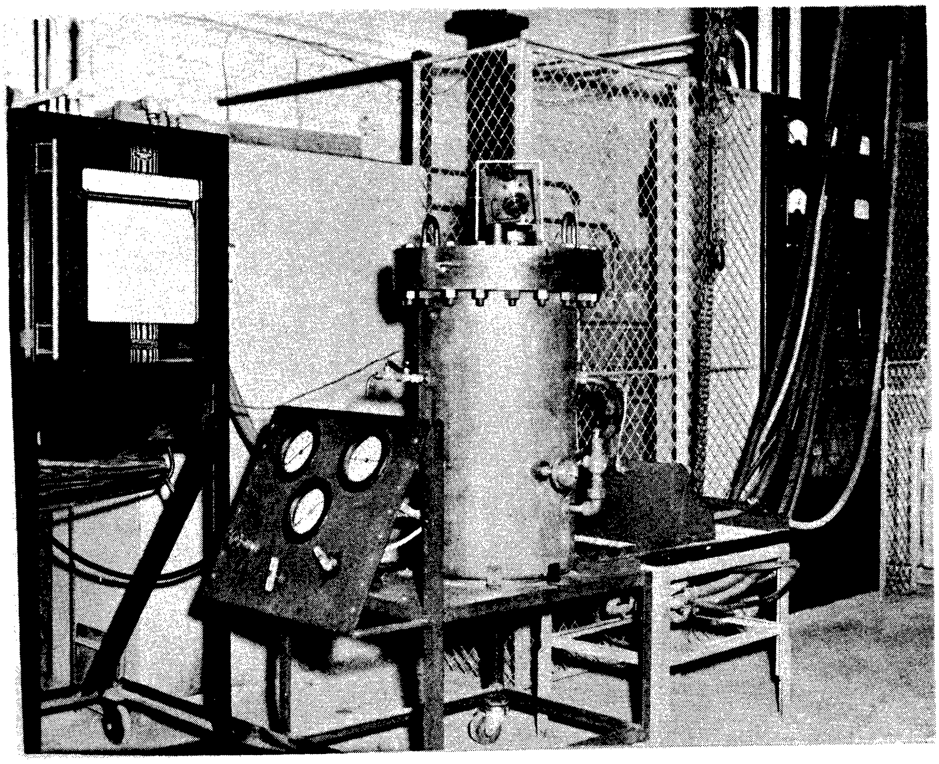

Figure 1. Experimental Pressure Chamber. The pressure chamber is shown, along with equipment for recording temperature, controlling power, and controlling pressure.

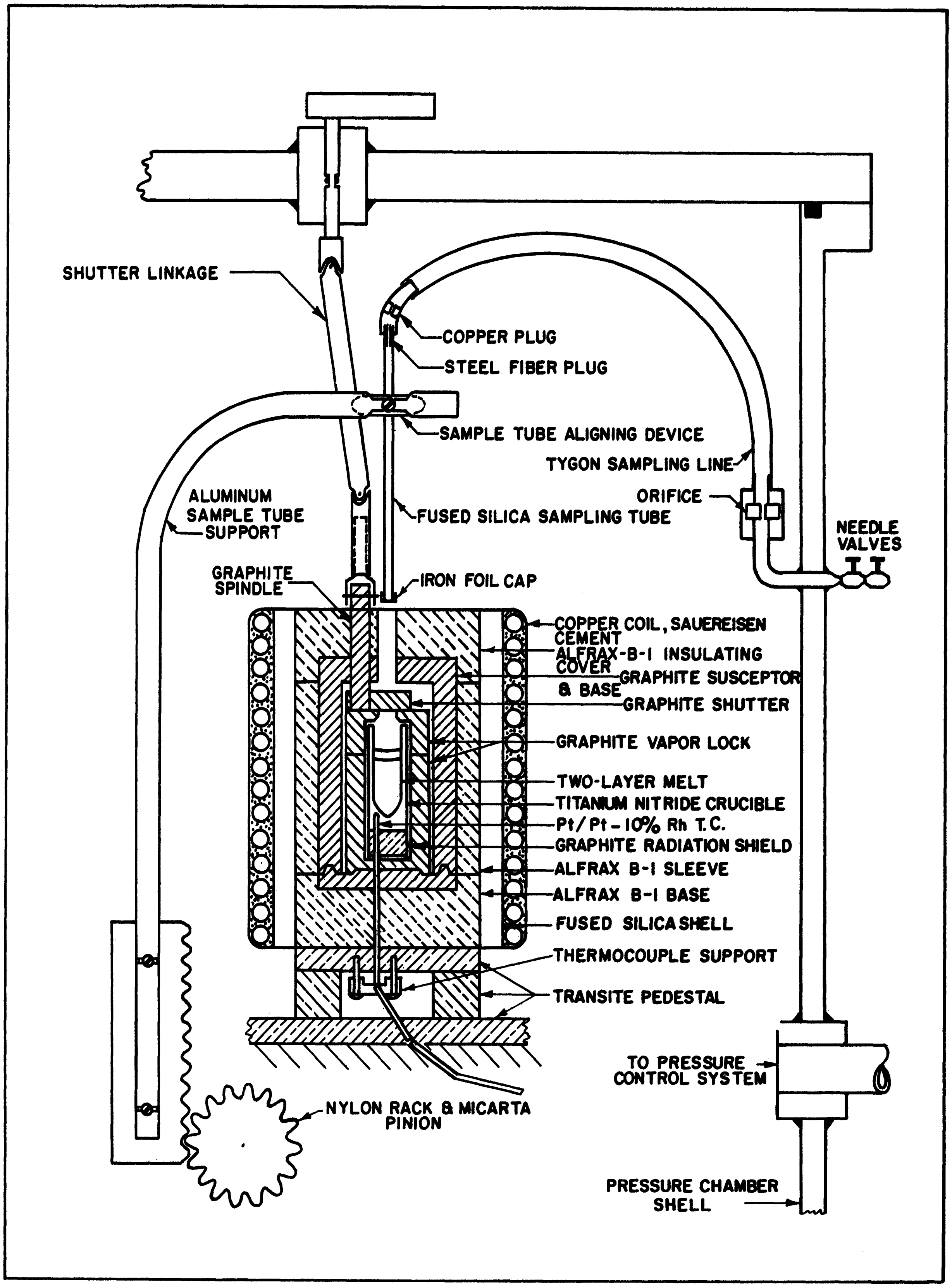

Figure 2. Furnace Arrangement. The interrelation of pressure chamber coil assembly, shutter turner and sampling device are shown in this schematic drawing.

a graphite shutter is remotely manipulated to uncover this hole, permitting the sampling tube to enter the melt. The crucible-vapor lock assembly is contained within a cylindrical graphite susceptor, which has holes in the top to permit entry of the sampling tube and to accommodate the spindle which turns the graphite shutter. The role of the susceptor is to heat the entire inner chamber and prevent calcium condensation. The inner parts of the coil assembly are shown progressively arranged in Figures 3 through 5.

2. Shutter Linkage

A mechanical linkage is used to rotate the shutter at the time of sampling, by means of a handle mounted in the cover of the pressure chamber. This linkage, shown in Figure 6, features two universal joints and a sliding joint. The universal joints provide the flexibility necessary to connect the linkage at the sliding joint when the furnace cover is lowered into position. Except for the graphite spindle which projects into the hot zone of the coil assembly, the shutter linkage is made from austenitic stainless steel and aluminum. A composite view of the shutter linkage and all parts of the coil assembly is shown in Figure 7.

3. Sampling Device

The sampling tube arrangement is illustrated in Figure 8. Samples of the iron-rich liquid are drawn into a fused silica tube. This tube is prepared by a meticulous cleaning, then coating the lower end with a colloidal dispersion of graphite in alcohol, wiring a piece of thin iron foil over the tip, and inserting a steel fiber plug of controlled length and weight into the upper end of the tube. The entire tube is then dried thoroughly over a Bunsen burner just before use. The iron foil serves to keep calcium vapor

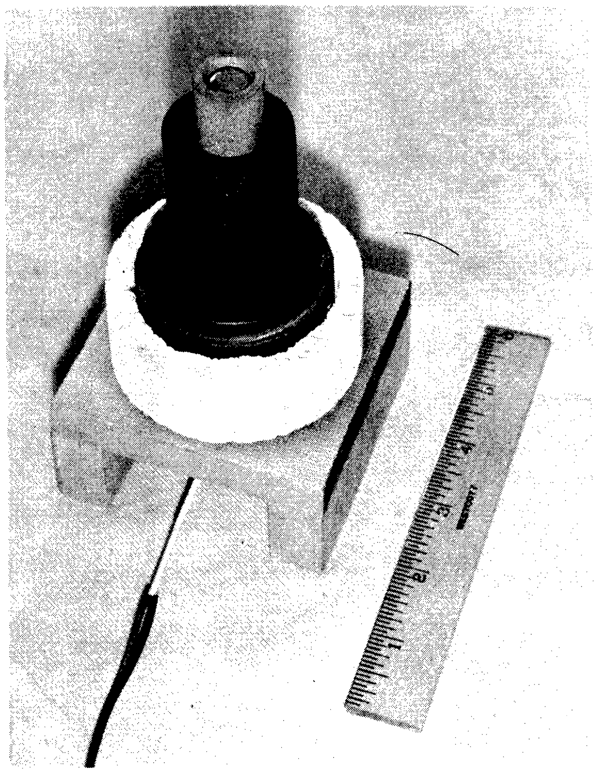

Figure 3.

Crucible in Position in Lower Section of Vapor Lock. The lower parts of the coil assembly are shown here, including thermocouple, pedestal, refractory insulating piece, susceptor base, lower section of vapor lock, titanium nitride crucible and self-contained charge.

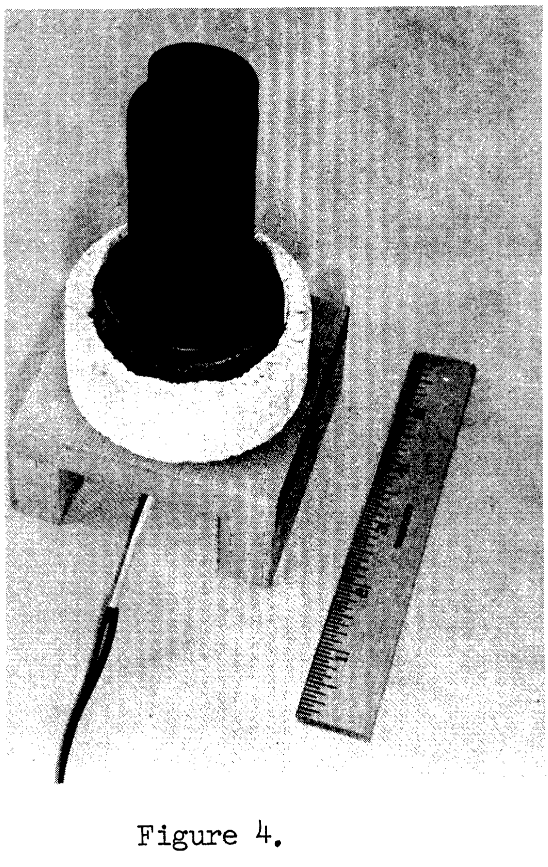

Figure 4.

Vapor Lock and Shutter Arrangement. The upper half of the vapor lock and the shutter have been added to the arrangement of Figure 3.

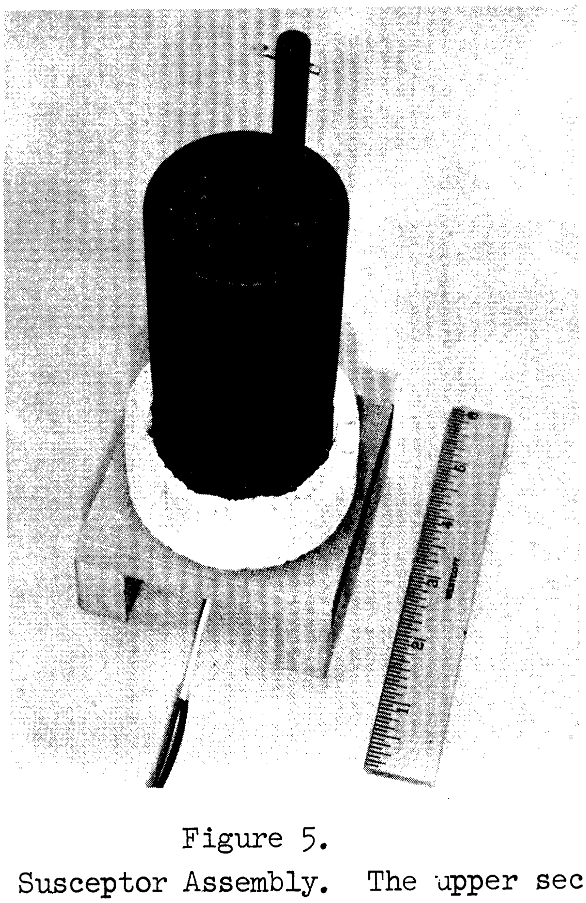

Figure 5.

Susceptor Assembly. The upper section of the graphite susceptor and the spindle for turning the shutter have been added to the arrangement of Figure 4.

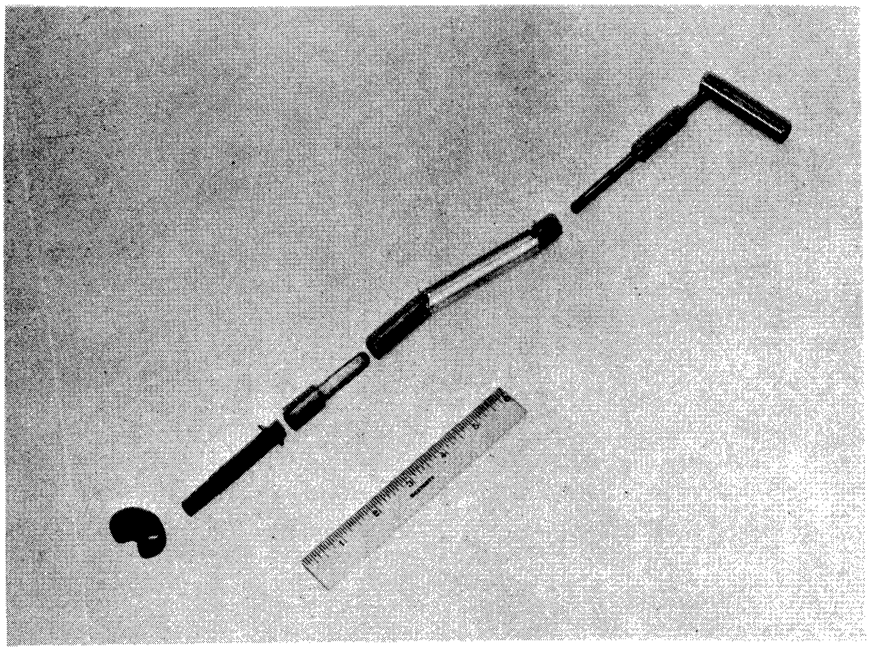

Figure 6. Shutter Linkage. The graphite shutter at the lower left is operated remotely by turning the handle at the upper end of the flexible linkage.

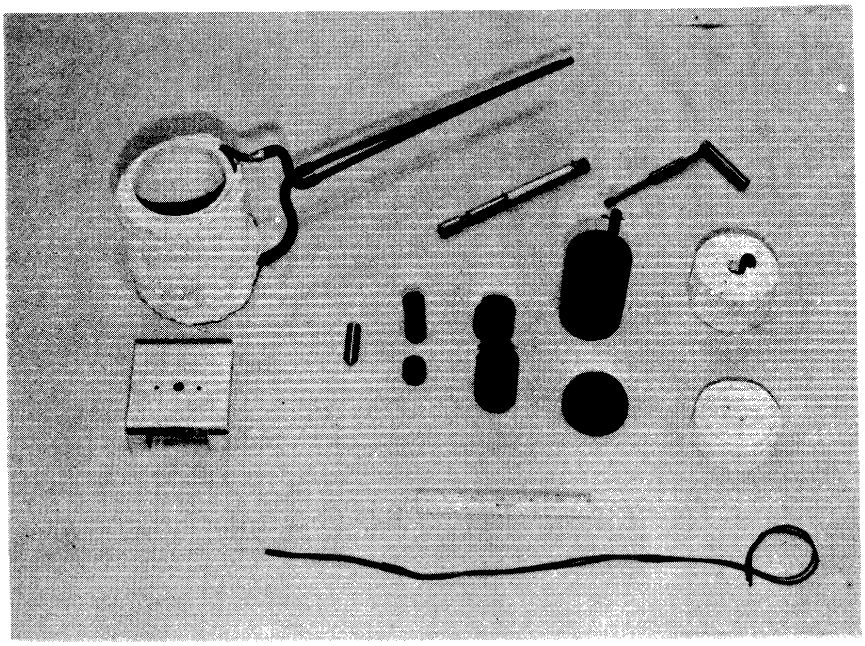

Figure 7. Coil Assembly Components and Shutter Linkage. Shown here are the induction coil pedestal, thermocouple, metal charge, crucible with radiation-shield base, vapor lock, susceptor, insulating pieces and shutter linkage.

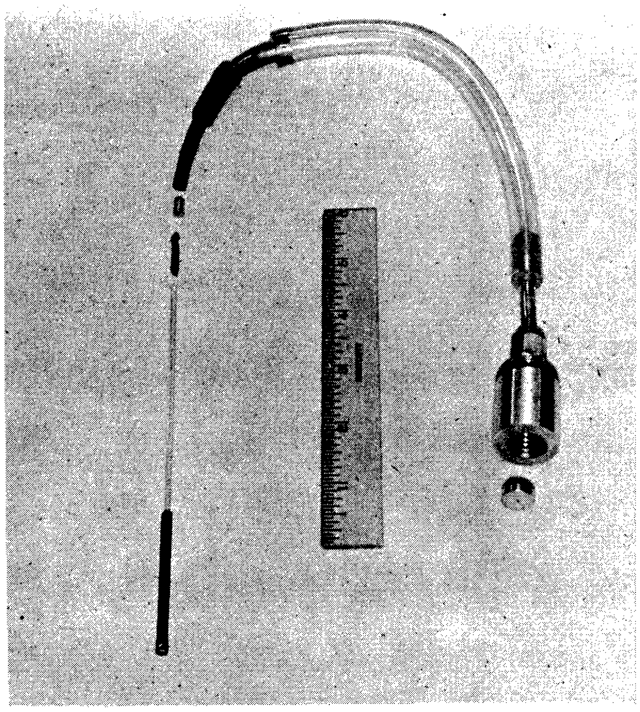

Figure 8. Sampling Tube and Suction Line. The assembly consists of a graphite-coated fused silica tube with iron foil over the lower end, a steel fiber plug, copper plug, flexible suction line, wall connection and orifice.

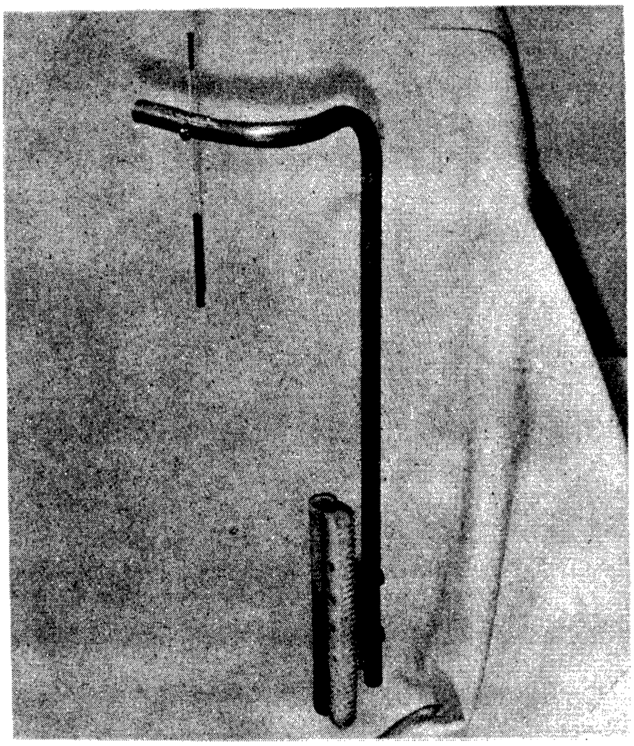

Figure 9. Sampling Tube Positioning Device. The sampling tube is carefully located in this device, which lowers the sampling tube into the melt at the time of sampling, and then withdraws it immediately after obtaining the sample.

out of the tube prior to sampling, and to prevent the calcium-rich liquid from entering the tube as it passes downward through this layer. The graphite dispersion is necessary to prevent the calcium-rich liquid from attacking the fused silica tube. Metal samples are chilled when they encounter the steel fiber plug, and this prevents them from vaporizing the rubber components of the suction line.

The metal samples are forced into the sampling tube by developing a pressure differential between the interior of the furnace and the sampling line. This is accomplished by bleeding argon from the sampling line to the atmosphere at the time of sampling. The pressure differential causes metal to rise rapidly in the sampling tube. The sampling rate is controlled by the use of an orifice and two needle valves, all in series, which retard the flow of the exit gas.

The device for lowering the sampling tube into the melt at the time of sampling is shown in Figure 9. This unit, which permits five degrees of freedom in aligning the sampling tube, is moved by a rack and pinion drive. The sampling tube is kept in position above the upper insulating piece until the time of sampling, when the tube is lowered into the iron-rich layer. Immediately after the sample is drawn, the tube is returned to its original position.

D. Preparation of Crucibles

In most experimental studies, crucibles which are commercially available can be used satisfactorily. Because of the extreme reactivity of calcium, however, such commercial crucibles were found unsatisfactory in this case. The performance of commercial crucible materials is described in this section, as well as the method for preparing titanium nitride crucibles. The method involves the steps of pressing, sintering and nitriding.

1. Performance of Commercial Crucibles

An extensive testing program was conducted to assess the suitability of commercially available crucibles for containing liquid calcium at temperatures above the melting point of iron. As a screening test, samples of the different crucible materials were tested in liquid lithium at 2500°F. Since lithium is somewhat more active chemically than calcium, such tests were used as an index of the ability of a refractory to withstand attack by liquid calcium at the higher temperature of this investigation. Tests were conducted by placing the refractory specimen and lithium within a hollow bomb-type iron crucible and inserting an iron plug. (This was done in a glove box.) After sealing the plug by arc-welding, the iron container was held for approximately 10 minutes at 2500°F in an induction furnace. The container was then sectioned and the refractory specimen was examined.

The results of these screening tests are presented in Appendix I. Briefly, all the commercial crucible materials tested were found unsatisfactory.

2. Selection of a Crucible Material

Of the possible classes of materials that might withstand attack by liquid calcium, the nitrides are of considerable interest because calcium is a relatively weak nitride-former. Titanium nitride is one of the most stable of the nitrides, and should therefore suffer little attack by metallic calcium. No experimental data were found concerning the resistance of titanium nitride bodies to attack by molten calcium. However, pure titanium nitride crucibles were found to be unattacked by molten cerium, a metal which, like calcium, is quite active chemically.(19)

3. The Effect of Titanium Hydride

In order to obtain impervious pure titanium nitride bodies by sintering, temperatures relatively close to the melting point of 5300°F are required since sintering must occur without the benefit of any liquid phase. At these temperatures, vaporization of the titanium nitride becomes quite appreciable. Furthermore, the use of very high sintering temperatures intensifies the technological problems associated with sintering.

The use of relatively large amounts of titanium hydride as an aid to sintering was suggested, and found to be quite effective.(20) Metallic titanium is formed at low temperatures from the decomposition of the titanium hydride, and greatly accelerates the sintering process at higher temperatures. A two stage sintering operation was developed by which the sintering process first is initiated at a temperature just below the melting point of the metallic titanium. During this time, the first stage of sintering, the metallic titanium is completely converted to TiN_x, where x is considerably less than unity. In the second stage of sintering, crucibles are heated to a temperature above the melting point of titanium to accelerate the densification process.

The optimum amount of titanium hydride was found to be 20 percent by weight.

4. Compacting of Crucibles

The powder from which crucibles are compacted is carefully prepared from the raw materials, the proportions of which are shown in Figure

10. Crucibles are pressed in a double-acting die which permits the base and walls of the crucible to be compacted separately, Figure 11. By careful control of the pressing operation, compacted crucibles having high sidewalls can be obtained free of cracks.

5. Sintering

Compacted crucibles are dewaxed at a final temperature of 475°F and are then placed in the induction sintering furnace shown in Figure 12, which was constructed for this purpose. A graphite susceptor is used to develop heat in the induction field, and contains the crucibles to be sintered. The susceptor is insulated by minus 100 - plus 150 mesh graphite. The water cooled cover contains a sight port for temperature measurement by an optical pyrometer.

After the system has been evacuated, the crucibles are held for 30 minutes at approximately 1200°F while the hydrogen from the decomposition of the titanium hydride is drawn off. The crucibles are then heated to 2950°F and held there for one hour. (This is termed first stage of sintering.) At this point argon is bled into the sintering furnace to a pressure of 5 psi (absolute) in order to reduce subsequent vaporization of the titanium nitride, and the crucibles are then heated to 3350°F. (This is termed second stage sintering.) After one hour at this temperature the furnace atmosphere is evacuated, power is turned off, and the crucibles are cooled under vacuum. The effect of sintering is illustrated in Figure 13.

Linear shrinkage and density measurements are made on all crucibles in order to keep the process in control. Also, crucibles are filled with distilled water and the drop in water level in one hour gives an index of

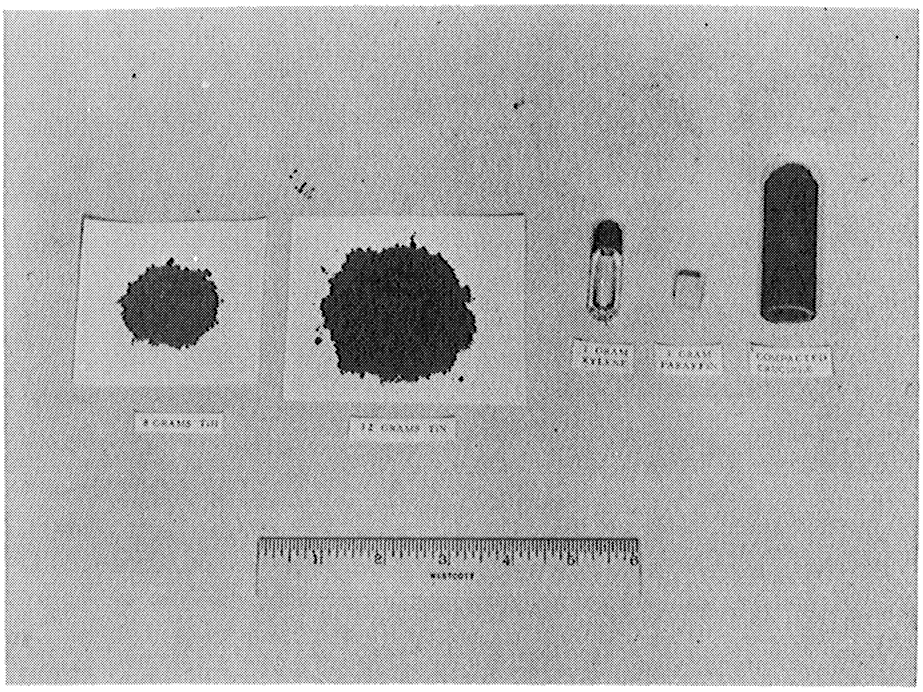

Figure 10. Constitution of a Compacted Crucible. The raw materials contained in a compacted 42-gram crucible are shown here, consisting of 8 grams of titanium hydride, 32-grams of titanium nitride, 1-gram of xylene and 1-gram of paraffin. A compacted crucible is shown at the right.

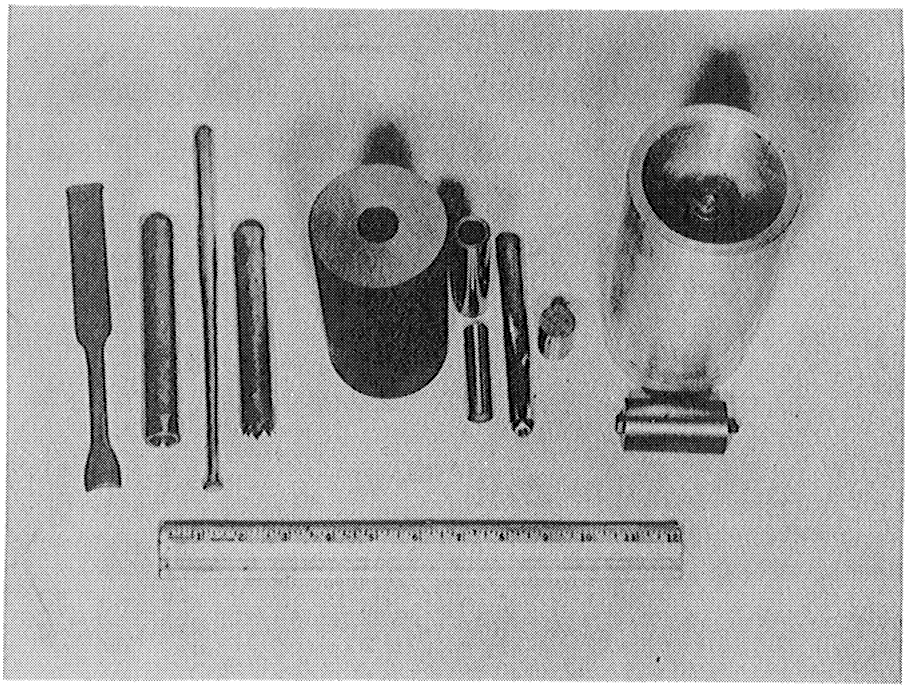

Figure 11. Crucible-Making Die and Accessories. The die components are shown in the center, with tools for assembling the die at the left and fixtures for disassembling the die at the right.

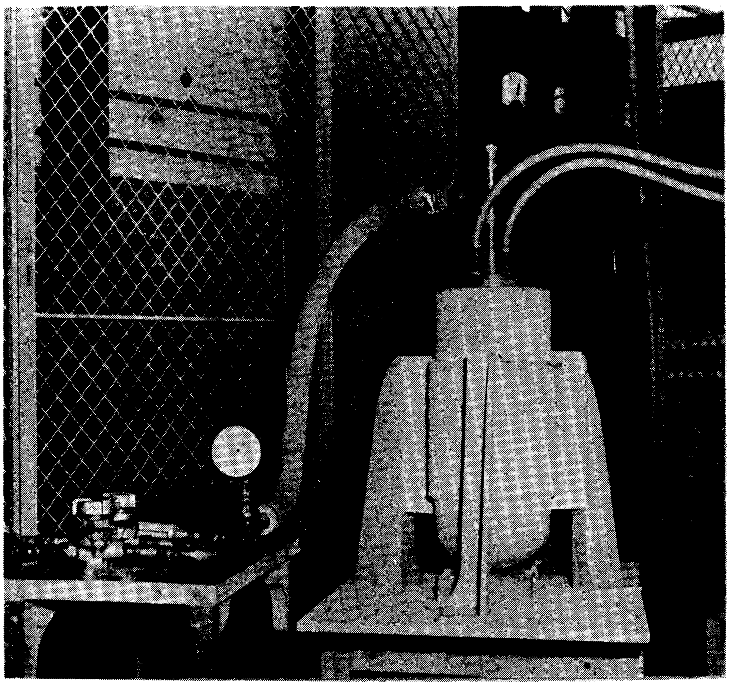

Figure 12. Induction Sintering Furnace. Fused-silica shell, induction coil, and water-cooled cover, with appropriate control equipment.

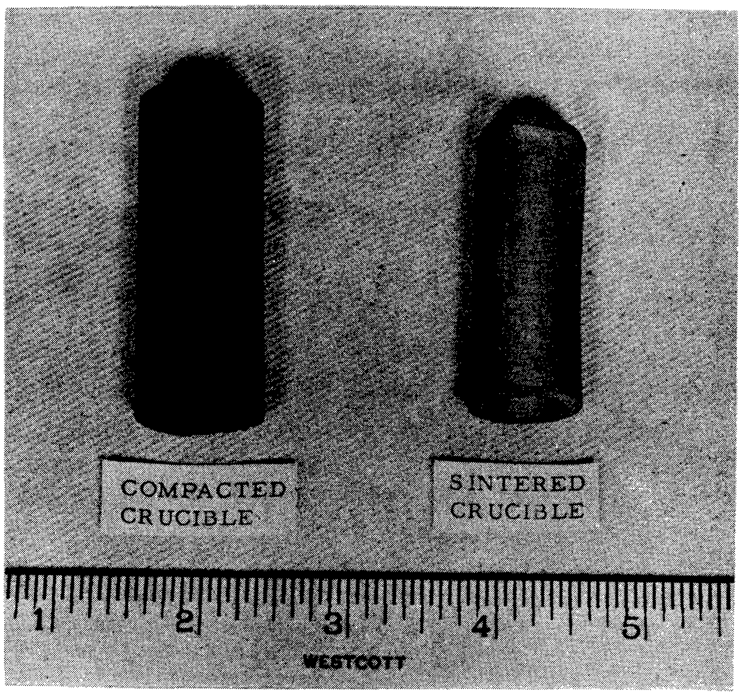

Figure 13. Comparison of Crucible Before and After Sintering. Extensive strinkage is evident, especially in the center of the sidewalk.

the ability of the crucible to contain liquid metal. The best crucibles show practically no absorption of the water. This latter test was especially valuable in perfecting the technique for making crucibles.

6. Nitriding

The addition of titanium (from titanium hydride) referred to above shifts the composition of the compound TiN_x rather far in the direction of titanium. Metallographic studies show that there is no free titanium present after sintering, all having been converted to titanium nitride of low nitrogen content. Crucibles cannot be used in this nitrogen-impoverished condition because they fail by thermal shock. Presumably a phase transformation occurs at low nitrogen levels, leading to failure.

Thermal-shock failures are completely eliminated by restoring the nitrogen level to a high value in a nitriding process. Crucibles are held in a purified nitrogen atmosphere at 2300°F for 48 hours. The nitrogen concentration approaches saturation in this treatment, and is accompanied by a color change of the titanium nitride from silver to gold.

7. Performance of Titanium Nitride Crucibles

Crucibles prepared by the foregoing procedure give very satisfactory service. The liquid calcium does not damage the crucible, the only effect of a chemical nature being that a small amount of the crucible dissolves in the melt. This results in a titanium concentration in the iron-rich layer of less than 0.3 wt% for most of the heats. The study of a special high-titanium heat shows that these low titanium levels have a negligible effect on calcium solubility.

A small amount of metal normally is absorbed by the crucible. For most heats of this investigation the loss is one gram or less.

The crucibles withstand the rapid heating and cooling of this investigation without any evidence of damage due to thermal shock.

E. Temperature Control

In any investigation of solubility accurate temperature measurements are desirbale. For this reason, a good deal of attention was given to reducing the absolute and relative errors in temperature measurements to a minimum. Since no satisfactory protective thermocouple tubes are available for immersion, the measurements are made using the crucible itself for protection as follows:

1. Method of Measuring the Temperature of the Melt

Temperature measurements are made with a platinum/platinum - 10% rhodium thermocouple located in the base of the crucible. This location is used in preference to the more conventional method of placing the thermocouple inside a protection tube immersed in the melt, for two reasons. First of all, no commercial protection tube would withstand attack by the calcium, and secondly, there is insufficient space in the small crucible for a thermocouple protection tube.

The location of the thermocouple is evident in the schematic drawing of Figure 2 and the photograph of Figure 14, showing the thermocouple hole in the base of a crucible and the insulated thermocouple. Crucibles are designed with a thick base to accommodate the thermocouple. Prior to dewaxing, an oval-shaped hole is carefully drilled to within 1/16 in. of the melt cavity of the compacted crucible. This hole is carefully shaped

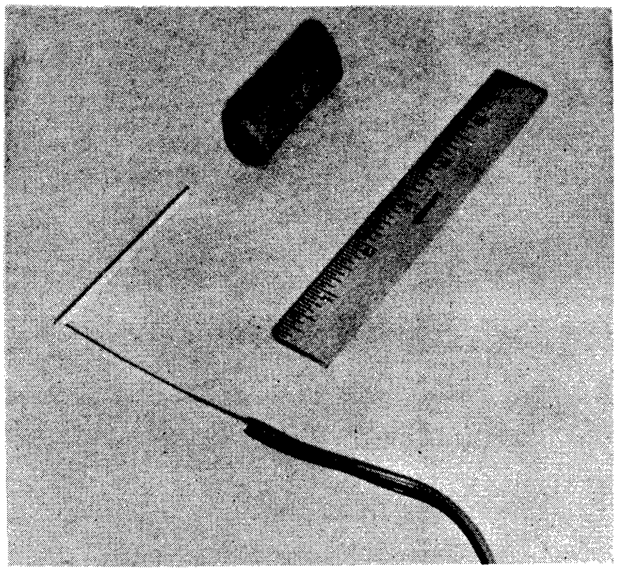

Figure 14. Location of Thermocouple. Bottom view of titanium nitride crucible, showing 5/16-in. deep thermocouple hole and insulated platinum/platinum - 10% rhodium thermocouple which is inserted into this hole.

to a standard template, which corresponds to the oval shape of the Triangle RR recrystallized alumina thermocouple insulator. After the crucible is sintered, the base is ground down until the thermocouple hole is exactly 5/16 in. deep. The thermocouple insulator has a 3/64 in. notch cut in the end, permitting the thermocouple bead to be recessed so that it does not touch the crucible.

The difference between the temperature at the control thermocouple and the temperature within the melt is shown for two separate calibration heats in Figure 15. These calibration heats involved a melt of Ferrovac 'E' iron equal in volume to the total volume of an iron-calcium melt. A thermocouple made from the same wire as the base thermocouple was located inside a protection tube immersed in the melt. Temperatures of the two thermocouples were recorded simultaneously after the temperature of the melt had stabilized at each of the three temperatures investigated. The calibration curves agree quite well, and indicate that the base thermocouple is 60°F below the temperature of the melt at 2925°F and 200 psig, the temperature and pressure respectively of this investigation.

2. Calibrations of Thermocouple Wire and Control Equipment

The thermocouple wire used in this investigation was calibrated against a platinum/platinum - 10% rhodium secondary standard, which had been previously calibrated by the National Bureau of Standards.

A thermocouple that had been used in an experimental heat was calibrated against an unused thermocouple made from the same wire to check for possible drift due to contamination during the course of a run, but no drift was detected. As a precaution against any slight contamination

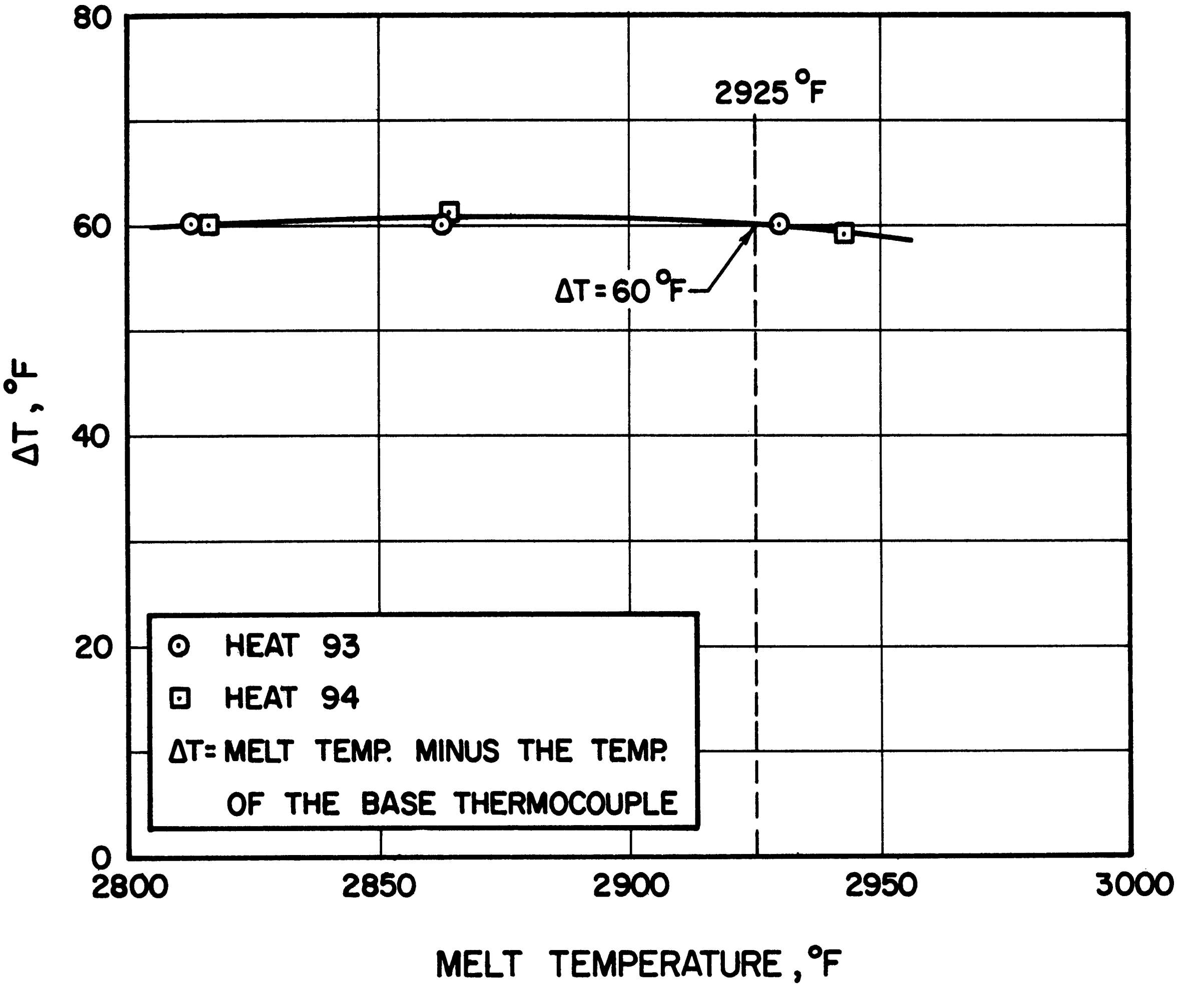

Figure 15. Calibration Curve for Base Thermocouple.

effects and possible mechanical damage, a one inch length at the bead end was cut off and discarded after each heat.

Immediately before each experimental heat the Leeds and Northrup Speedomax Temperature recorder was calibrated against a Leeds and Northrup portable precision potentiometer. This potentiometer had in turn been calibrated against an Eppley standard cell.

3. Accuracy of Temperature Control

The experimental melts were maintained at 2925°F during the equilibration period by adjusting the power input manually. When this small source of error is considered with other possible sources of error, the temperatures of all heats in this investigation are estimated to lie within 15°F of 2925°F. For the majority of heats, the maximum error is estimated to lie between 5° and 10°F.

F. Conduct of Experimental Heat

1. Raw Materials

The calcium, iron, and alloying elements employed in making the investigation are specially selected materials of high purity, Table I. The calcium granules are remelted into an ingot and hot rolled to obtain solid bars more suitable for the preparation of charges.

Carbon is added in the form of carbon-saturated iron containing approximately 4.3 wt% carbon. This material is prepared by vacuum melting the Ferrovac 'E' iron in a crucible made of Graphite 'G' type Graphite.

2. Preparation of Charges

It is necessary to carefully fit the melting stock into the crucible to obtain an adequately-sized melt, since it is not experimentally

TABLE I

CHEMICAL ANALYSIS OF RAW MATERIALS

MATERIAL	SUPPLIER	MAJOR IMPURITIES			
Grade 1 special purity Calcium granules	Dominion Magnesium, Ltd.	N_2		0.011	percent
		Mg	less than	0.01	percent
		Al		0.0028	percent
		Mn		0.002	percent
		Fe		0.006	percent
Ferrovac 'E' vacuum-melted iron	Crucible Steel Company	Ni		0.035	percent
		Si	less than	0.03	percent
		Cu		0.01	percent
		Cr	less than	0.01	percent
		S		0.005	percent
		C		0.004	percent
		Al	less than	0.003	percent
		P		0.002	percent
		Mn		0.001	percent
		Mg	less than	0.001	percent
		Ca	less than	0.001	percent
99.99% aluminum	Aluminum Company of America	Cu		0.002	percent
		Si		0.002	percent
		Fe		0.001	percent
Carbon (Graphitite 'G') 99.5% + purity	Graphite Specialties, Inc.				
Gold Sheet	J. Bishop and Co.	Ag	less than 0.02 percent total		
		Cu			
		Ca			
		Mg			
		Si			
Vacuum remelted Carbonyl nickel	Mond Nickel, Ltd.	Co	less than	0.01	percent
		Mo	less than	0.01	percent
		Mn	less than	0.01	percent
		Zr	less than	0.01	percent
		C		0.005	percent
		Si	less than	0.005	percent
		Ti	less than	0.005	percent
		S		0.024	percent
Solar Grade Silicon	E. I. DuPont DeNemours and Co.	No impurities present in any significant amount.			

feasible to add additional materials to the charge after meltdown as for open-air melts. The weight of alloying element was selected to provide for equal molar concentrations of the alloying element in the calcium-rich and iron-rich layers. In addition, a slight allowance is provided for preferential absorption of the alloying element by the titanium nitride crucible, since the alloying element melts down or is dissolved before the last iron has melted. By use of Vegard's law, the weight of the iron-base melt is calculated to correspond to a volume in the solid state of 2.85 cm^3 at room temperature. For most heats the iron-rich layer weighs approximately 22 grams. The calcium-rich layer is calculated to have a final solid volume of 0.5 cm^3, allowing for some loss by evaporation.

The calcium and alloying element are contained within a hollow bomb-type iron crucible, Figure 16. After the charge components are carefully weighed and cleaned, the calcium and alloying element are loaded into the iron crucible and the tapered iron plug is pressed in place. This arrangement protects the calcium from oxidation, and prevents any vaporization loss of the calcium until the iron container has melted.

3. Furnace Assembly and Operation

After the charge, crucible, and all components described in previous sections have been assembled in the pressure furnace, the sampling tube is carefully aligned above the coil assembly. The furnace lid is then bolted in place and the furnace is evacuated for two hours, flushed with argon, and then evacuated for one more hour. During operation, argon is admitted after the temperature has reached 1500°F, and the furnace is pressurized to 200 psig. (This pressure, which is considerably higher than

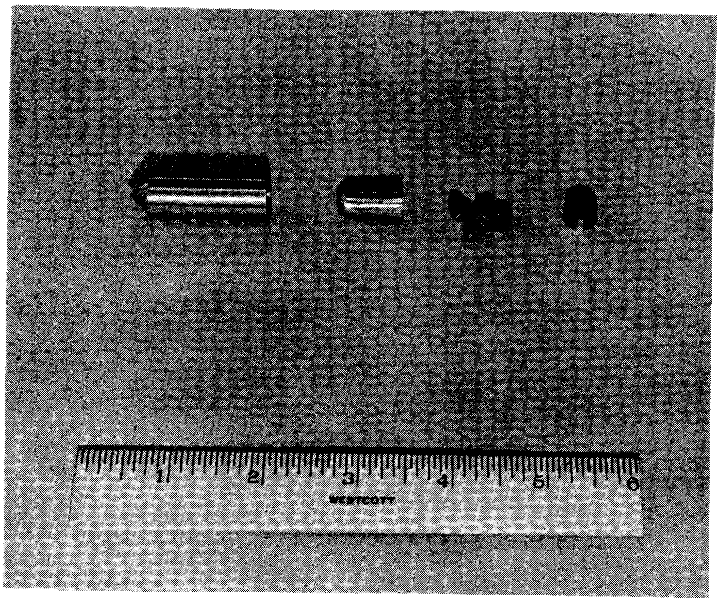

Figure 16. Components of a Typical Charge. The components of the 5 At.% silicon charge are shown, which include from left to right the iron-bomb type container, the calcium, the silicon, and the iron plug.

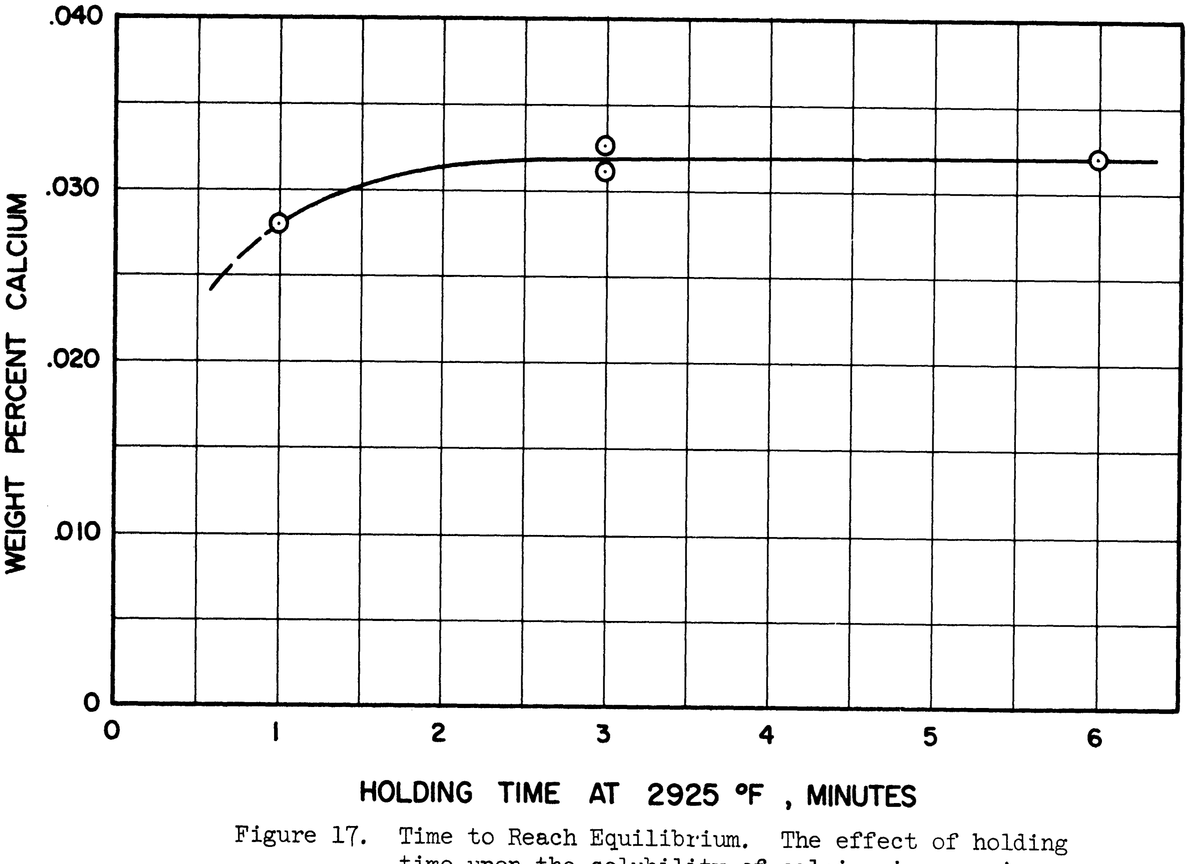

Figure 17. Time to Reach Equilibrium. The effect of holding time upon the solubility of calcium in pure iron at 2925°F is shown here.

the vapor pressure of calcium at 2925°F, is chosen to retard calcium vaporization.) The melt is held for three minutes at 2925°F, a period which is sufficient for attaining equilibrium, as seen in Figure 17. This relatively rapid rate of equilibration is quite consistent with the rate observed by Trojan and Flinn in the magnesium-iron-carbon system.(12)

At the conclusion of the equilibration period, the sampling tube is lowered into the iron-base melt, a sample is drawn, and the tube is returned immediately to its starting position.

Samples are solid, smooth, shiny, and free from any calcium that was not in the iron-rich layer. In every case a calcium-rich layer is present in the crucible at the completion of a run. The appearance of a two-layer melt from a typical heat is shown in Figure 18.

G. Chemical Analysis

The determination of calcium in iron-base samples is not routine because relatively little analytical work has been done in this field. Furthermore, because a high degree of accuracy seemed desirable in this investigation, it was decided to develop and perform the analytical procedures as an integral part of the work.

Two factors serve to complicate the analysis for calcium. In the first place, the chemical nature of calcium is such that it cannot be isolated directly from the other elements present, due to the high solubility of calcium compounds in aquaeous solutions. This requires that all other elements must first be removed before the concentration of calcium can be determined. The second complicating factor is the low level of

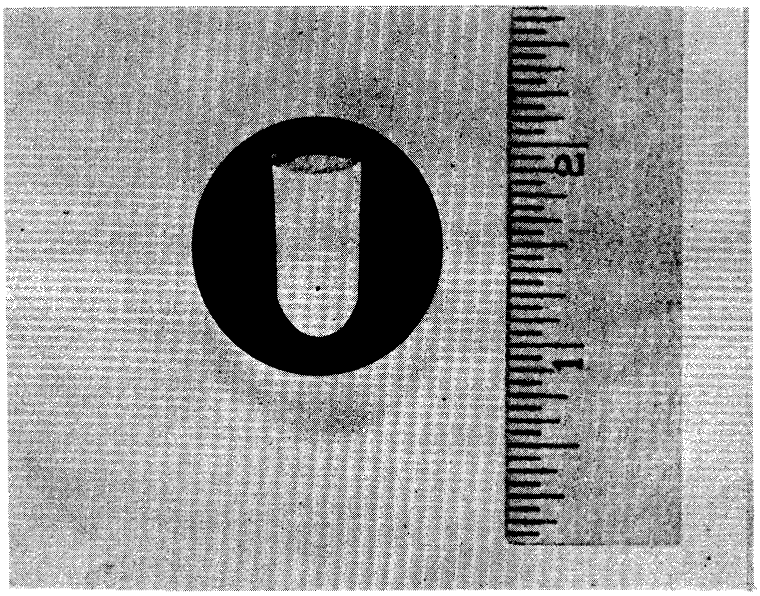

Figure 18. Two-Layer Melt. This photograph shows the calcium-rich layer (upper) and the iron-rich layer (lower) which are presented at the completion of a typical experimental run. No sample was drawn from this melt, and therefore the iron-rich layer is the same size as in a typical melt just before sampling.

calcium concentrations encountered in this investigation. This intensifies problems such as contamination, co-precipitation, interference by trace elements, and accuracy of measurements. These effects are less troublesome at concentrations two or three orders of magnitude higher.

In this section, first the basic procedure for simple iron-calcium samples is outlined, then the modifications necessary for samples containing the various alloying elements, and finally the analysis for the various alloying elements. More detailed descriptions of the procedures, along with results of a reproducibility study are presented in Appendix II.

1. Basic Procedure for Unalloyed Samples

In the analysis of the simple unalloyed samples, as well as in the procedures for alloyed samples, the removal of interfering elements by precipitation processes is avoided wherever possible. This is because a significant part of the trace calcium present can be lost by occlusion, absorption, or co-precipitation during such a process. Solvent extractions provide a way of avoiding certain precipitation processes, and the basic procedure involves two solvent extractions. The weight of the iron-base sample is 1.5 grams.

In the first solvent extraction, iron is removed with isopropyl ether. Any remaining iron, as well as the titanium dissolved from the crucible, is removed by the use of cupferron (ammonium N-nitrosophenylhydroxylamine) and diethyl ether in a second solvent extraction. Calcium is then determined by titrating with 0.001 M versene (ethylenedinitrilotetracetic acid disodium salt) at a pH of 10.5, in the presence of eriochrome black T indicator. A study of reproducibility for this basic procedure showed the standard deviation to be 4 percent of the amount analyzed at the 0.05 percent calcium level, an accuracy of ±0.002 percent calcium at this level.

2. Procedures for Alloyed Samples. The basic procedure just described is quite compatible with the removal of the alloying elements aluminum, carbon, gold, nickel and silicon. Aluminum is removed by a second cupferron extraction at a pH of 2.5 to 4.5, carbon is removed by filtration, gold is extracted simultaneously with iron during the isopropyl ether extraction, while nickel is electrodeposited from an ammoniacal solution. Samples containing silicon are by far the most difficult to analyze for calcium. Silicon is removed as hydrated silica by two dehydration-and-filtration operations, followed by a procedure involving a cation exchange resin. Here the calcium is collected on the resin while the trace silica still in solution passes through the column and is discarded. Then the calcium is eluted from the column and analyzed.

Three standards, covering the complete range of alloy concentration under test, along with a blank solution, are analyzed with each set of unknowns.

Unknowns are analyzed for gold and nickel gravimetrically as a part of the procedure. Aluminum, carbon and silicon are determined by commercial laboratories previously found reliable for this type of investigation.

DISCUSSION OF RESULTS

The data for the solubility of calcium in pure iron and in the various iron alloy systems are presented in Table II and Figures 19 - 23.

It appears logical to divide the discussion of these data into three principal sections:

1. Review of the data per se and in the light of previous investigations.

2. The engineering applications of the solubility data regarding refining reactions in actual process metallurgy.

3. The significance of the data in relation to certain theoretical concepts of liquid solutions.

A. Review of the Data

The data for the solubility of calcium in pure iron and in iron containing increasing amounts of the various alloying elements show regular changes in calcium concentration with increasing amounts of alloying element.

Four of the elements raise the solubility of calcium sharply while gold lowers solubility strongly.

1. Solubility of Calcium in Pure Liquid Iron at 2925°F

The restricted solubility of calcium in liquid iron at 2925°F, 0.032 wt% as shown by the average of duplicate heats, Figure 17, is consistent with the relatively large size of the calcium atom. Also, the immiscibility predicted by Hildebrand and Scott and by Mott for the

TABLE II

CHEMICAL ANALYSIS OF EXPERIMENTAL HEATS

Heat No.	Calcium in the Iron-rich Layer (Wt.%)	Alloying Element in the Iron-rich Layer (Wt.%)
Pure Iron		
99	0.032	----
102	0.031	----
Aluminum Series		
125	0.040	1.07
126	0.052	2.69
127	0.063	4.99
128	0.148	10.61
Carbon Series		
122	0.044	0.37 (1)
123	0.052	0.74 (1)
124	0.033	1.50 (1)
Gold Series		
118	0.026	0.19
118(2)	0.025	----
119(2)	0.014	0.36
120	0.004	0.90
121(2)	0.002	8.52
Nickel Series		
115	0.041	2.13
112	0.051	5.14
113	0.082	10.35
114	0.207	19.71
Silicon Series		
107	0.037	1.11
104	0.059	2.59
105	0.089	5.17
106	0.360	10.50

(1) Carbon concentrations obtained by subtracting average carbon pickup from the sampling tube, 0.04%, from the analyzed value.

(2) Samples cut from melt.

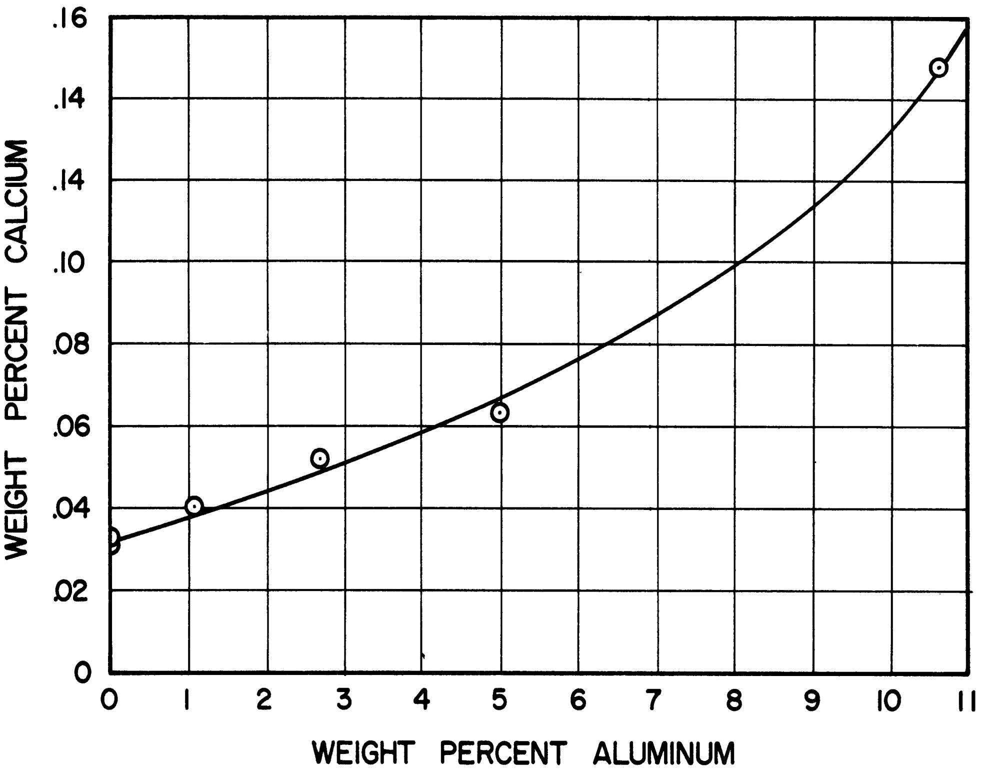

Figure 19. Effect of Aluminum Upon the Solubility of Calcium in Liquid Iron at 2925°F.

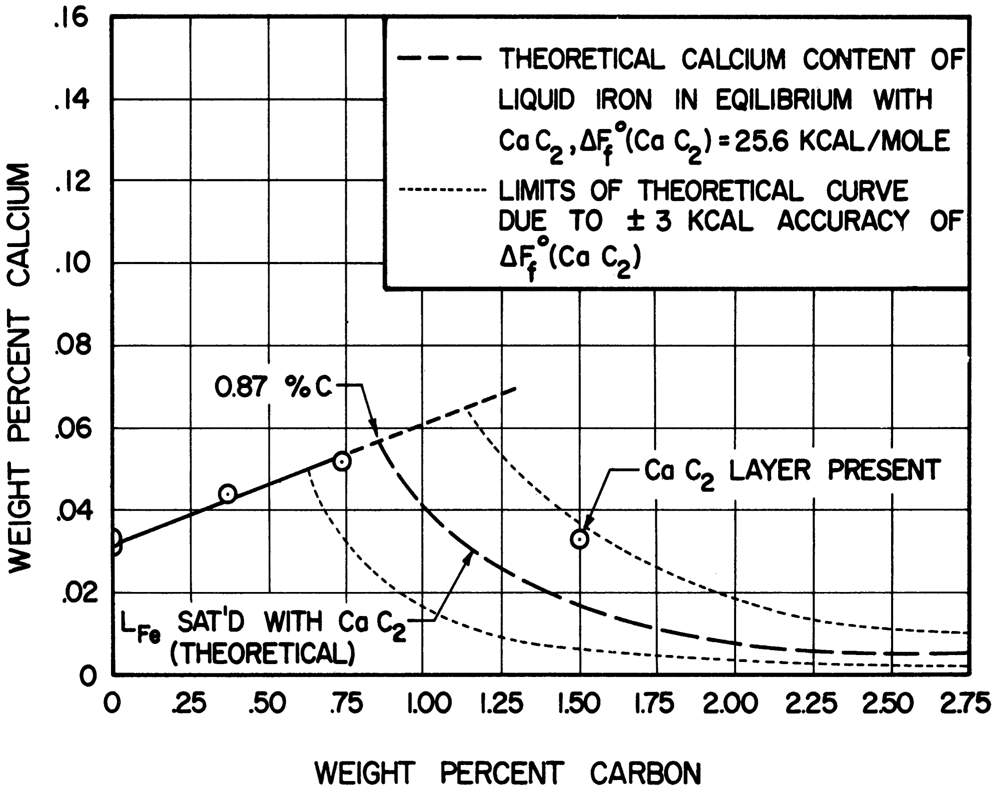

Figure 20. Effect of Carbon Upon the Solubility of Calcium in Liquid Iron at 2925°F.

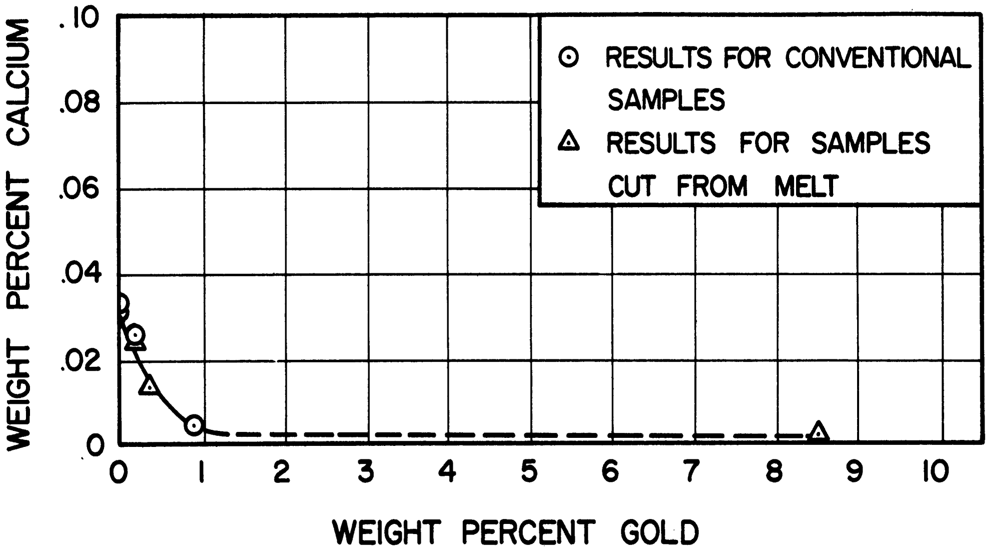

Figure 21. Effect of Gold Upon the Solubility of Calcium in Liquid Iron at 2925°F.

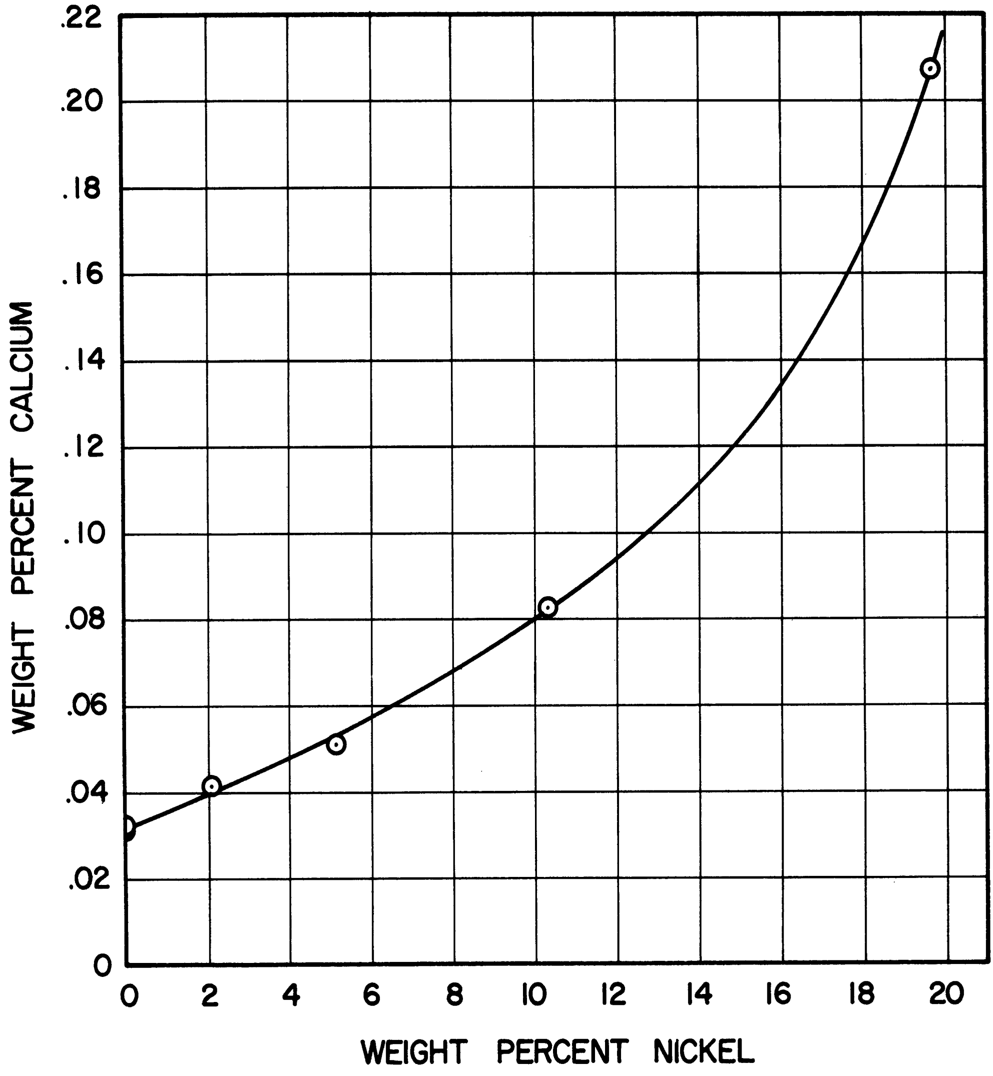

Figure 22. Effect of Nickel Upon the Solubility of Calcium in Liquid Iron at 2925°F.

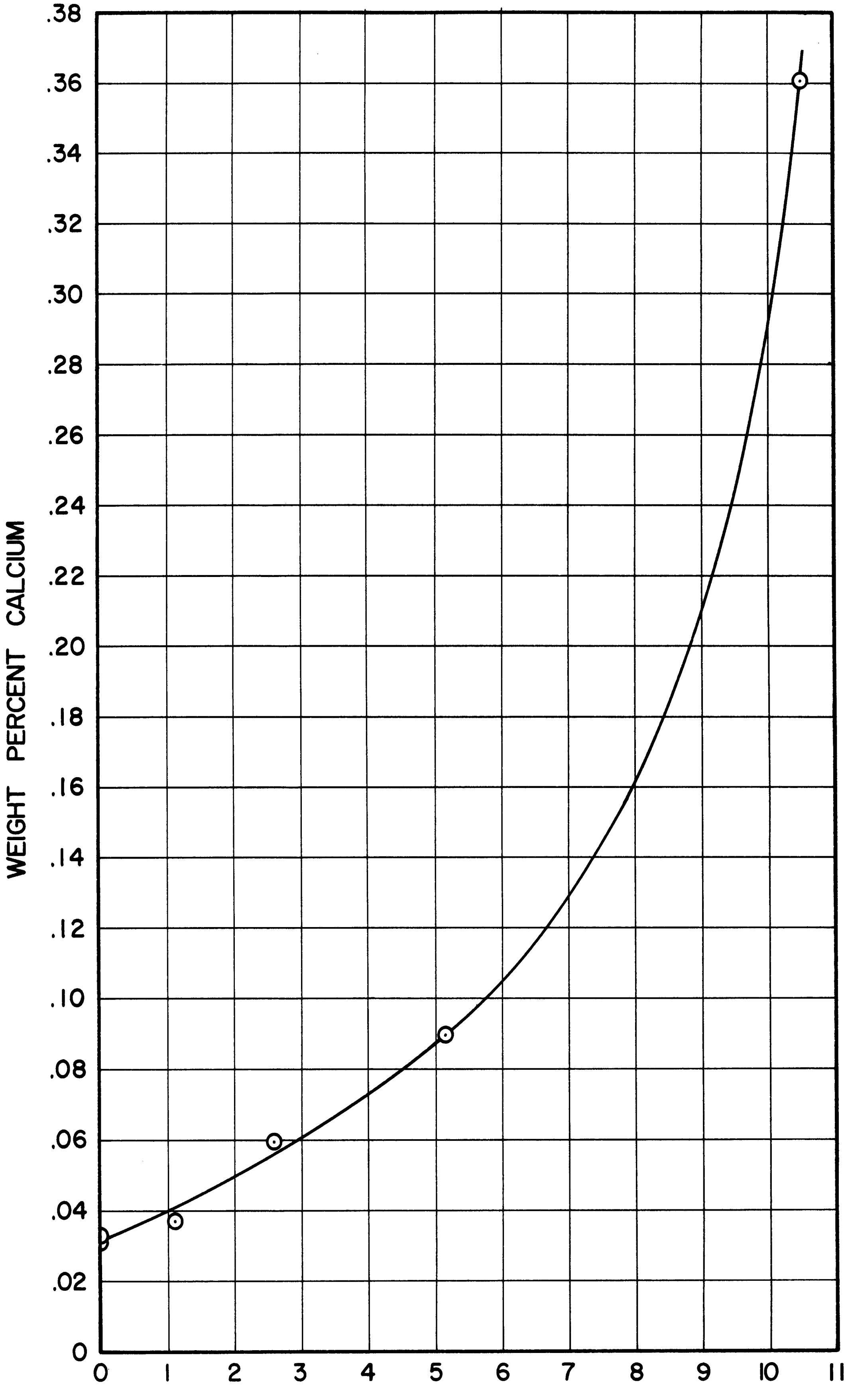

Figure 23. Effect of Silicon Upon the Solubility of Calcium in Liquid Iron at 2925°F.

iron-calcium system is confirmed.(9,10) Furthermore, the measured solubility of calcium corroborates the order-of-magnitude upper limit of 0.1 weight percent calcium at 3272°F, calculated from the data of Philbrook et.al.(11)

The data refer of course to calcium solubility at 2925°F in the presence of a calcium-rich layer at 200 psig in a system containing argon. However, the solubility of calcium should be the same at any pressure sufficient to prevent the calcium-rich layer from boiling away, for reasons discussed previously. At pressures insufficient to maintain a calcium-rich layer, the calcium concentration should decline. Under such conditions the phase rule variance at any temperature and pressure will be one, and the calcium concentration in the iron will be a function of the calcium concentration in the gaseous phase at the surface of the liquid iron.

2. Effects of Alloying Elements Upon the Solubility of Calcium in Liquid Iron at 2925°F

The changes in the solubility of calcium in liquid iron with the additions of various alloying elements may now be considered, Table II.

a. Aluminum

Additions of aluminum increase strongly the solubility of calcium in liquid iron from the average value of 0.032 wt% in pure iron, to 0.148 wt% in iron containing 10.61 wt% aluminum, an increase of nearly five times, Figure 19.

b. Carbon

The solubility of calcium in liquid iron rises quite sharply initially as carbon is added to the system, Figure 20. At 0.74 wt% carbon the corresponding calcium concentration in liquid iron is .052 wt%. At the highest carbon level in this series, Heat 124, 1.50 wt% carbon, the calcium concentration is less than at the two lower carbon levels. This effect in the high carbon heat is accompanied by the formation of a layer of calcium carbide, and the lower solubility may be readily explained by the presence of this new phase.

At the temperature of this investigation, the theoretical carbon level at which calcium carbide should form in the presence of a calcium-rich layer is approximately 0.87 wt% carbon. This is the carbon concentration at the junction in Figure 20 of the extended calcium solubility curve and the theoretical curve for the calcium concentration in an iron-rich layer saturated with calcium carbide. The theoretical curve is calculated for $\Delta F_f^\circ(CaC_2)$ = -25,600 cal/mole for calcium in the liquid state, and using the data of Rist and Chipman for the activity of carbon in iron.(21,22) The effect of carbon upon the activity coefficient of calcium in iron observed experimentally in this study, as well as the small mutual effect of calcium upon the activity coefficient of carbon in iron are taken into account, using the relationship considered by Ohtani and Gokcen for interaction parameters:(23)

$$\epsilon_2^3 = \epsilon_3^2 .$$

This equation is valid when the concentrations of the two solute species in the ternary system approach zero, and is considered reasonably accurate for the present calculation.

At this unique carbon concentration where the two curves meet, calcium carbide could exist at equilibrium with the two liquid phases and the vapor phase at 2925°F. The phase rule indicates that one of the phases must be removed, however, before the carbon concentration of the iron melt becomes any higher under equilibrium conditions. In the presence of excess iron, as in these experiments, this could take place by the disappearance of the calcium-rich liquid by reaction with carbon to form calcium carbide. The equilibrium calcium concentration thus drops very sharply with increasing carbon content.

The lower calcium concentration of Heat 124 is related to the shape of this theoretical curve. True equilibrium is not attained because a calcium-rich layer is still present at the conclusion of the heat. The calcium carbide may be considered as separating the melt into two systems, with the calcium carbide attempting to maintain dynamic equilibrium with the calcium-rich layer (and vapor phase) on one side and with the iron-rich layer on the other. In view of the relatively close agreement between the high carbon data point and the theoretical curve, the couple between the iron-rich layer and calcium carbide is considered to be relatively close to dynamic equilibrium.

c. Gold

Additions of gold cause drastic reductions in the solubility of calcium in liquid iron, Figure 21. This effect is presumably related to the highly preferential distribution of gold in the calcium-rich layer, causing a very sharp reduction in calcium activity. An extreme indication of the preference of gold for the calcium rich layer is that at the highest gold level studied, nominally 20 atomic percent in the iron, the high-calcium layer sinks below the iron-rich layer, even though the density of iron is five times that of calcium.

The high preference of gold for the calcium-rich layer is presumably due to deviations from ideality in the gold-iron and gold-calcium systems. Gold is expected to exhibit strong positive deviations from Raoult's law when dissolved in iron, in the manner of copper. This is consistent with the similarity between the gold-iron and copper-iron phase diagrams. Furthermore, the presence of six intermetallic compounds in the gold-calcium system indicates strong negative deviations for gold in this system. Deviations of this type could easily result in a 500:1 partition of gold in calcium relative to iron.

A conventional sample was not obtained from the iron-base layer of the high-gold heat, as well as from the second heat in the gold series. The analyses for these heats are taken from samples cut from the melt, as noted in the graph. To determine whether the melt sample was useful, a melt sample and a conventional sample were analyzed from the lowest gold heat. The data for these samples agree quite closely with each other, Figure 21, indicating that some confidence may be placed in the melt samples.

d. Nickel

Additions of nickel raise the solubility of calcium in liquid iron strongly, Figure 22. The 0.207 wt% Ca level at 19.71 wt% nickel represents a six-fold increase over the solubility in pure liquid iron.

e. Silicon

The highest calcium concentration in iron of this investigation is due to the addition of silicon, as seen from Figure 23. Calcium solubility is 0.360 wt% at 10.50 wt% silicon, an order-of-magnitude increase from the value for pure iron.

B. Engineering Significance of the Solubility of Calcium in Liquid Iron

In view of the present importance of calcium alloys and the possible use of metallic calcium as a refining agent in steelmaking, appreciable solubility of calcium in liquid iron is of considerable importance. The consequences of complete insolubility would be that when calcium vapor or metallic calcium were in contact with the liquid metal, any refining action would be confined to the contact surface layer. Because calcium can dissolve to a limited extent in liquid iron, however, the refining process should be much more effective. Calcium atoms can diffuse into the liquid steel and remove dissolved impurities at a considerable distance from the boundary of the calcium-rich phase. The potential use of calcium as a refining agent may now be considered first for open systems and then for pressurized systems. Finally, the importance of the immiscibility between liquid iron and liquid calcium is reviewed.

1. Calcium as a Refining Agent in Open Systems

In an open system, the vapor pressure of calcium as a function of temperature must be considered, Figure 24. Because of the high vapor pressure of calcium, any liquid calcium would boil away rapidly in the temperature range shown, 2800 to 3000°F. If the activity of calcium in the pure liquid state is taken as unity, the maximum value of calcium activity at 1 atmosphere, a^*_{Ca}, is the ratio of atmospheric pressure to the vapor pressure,

$$a^*_{Ca} = \frac{14.7}{\text{V.P. of Ca}} . \qquad (5)$$

The curve for a^*_{Ca} is included in Figure 24. Boiling of the calcium can be prevented, therefore, by keeping the calcium activity below a^*_{Ca}. This

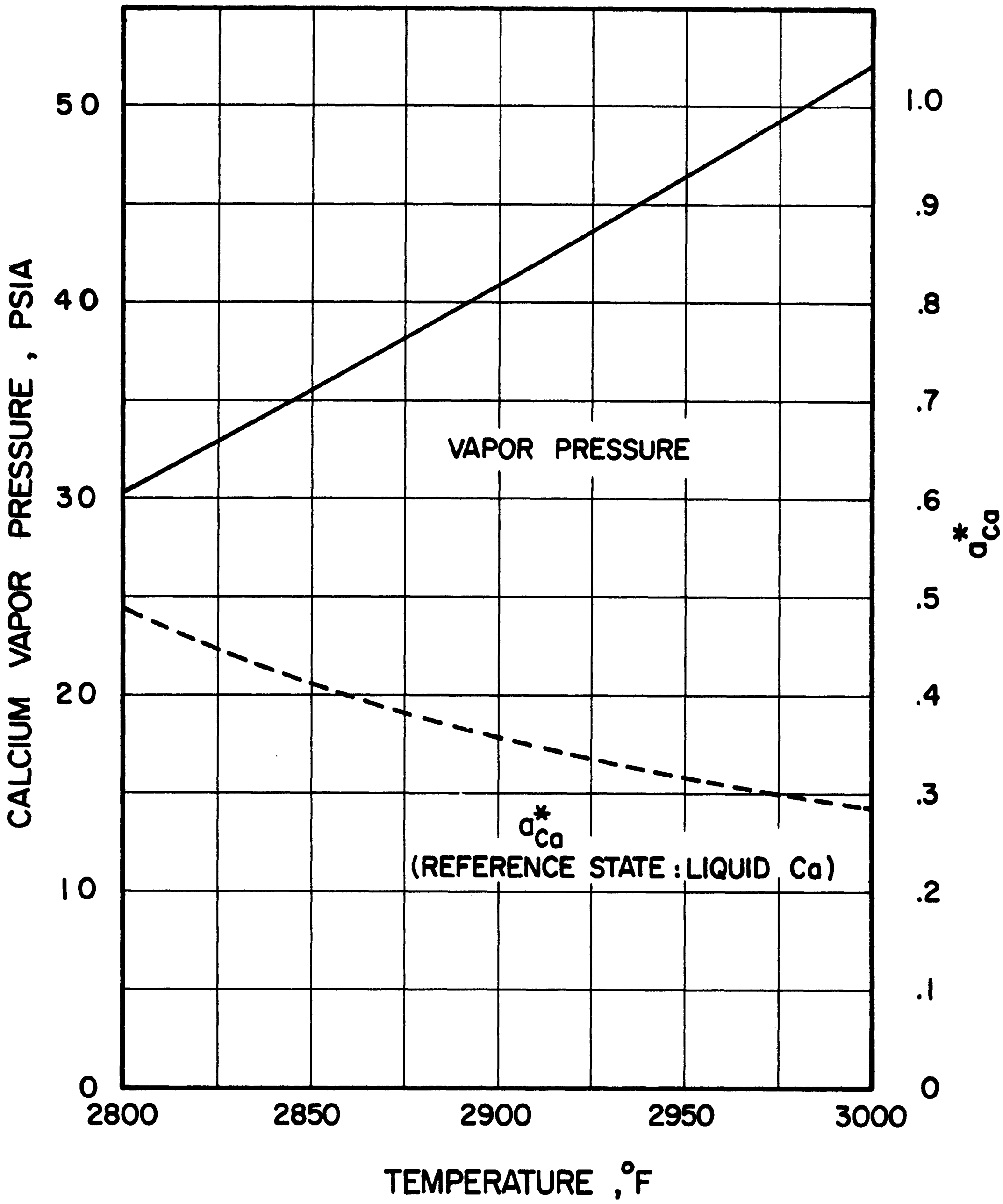

Figure 24. Vapor Pressure of Calcium at Steel-making Temperatures.

can be accomplished by employing an intermetallic compound with an element X, $Ca_m X_n$, for which the calcium activity is below a^*_{Ca}. It must be borne in mind that if element X dissolves in the liquid iron before the calcium does, then the calcium would attempt to develop its equilibrium vapor pressure and boil away. Therefore if element X is highly soluble in liquid iron, the concentration of calcium in X should be kept quite low to prevent boiling. If element X is less soluble in iron, as in the case of carbon, then boiling away of the calcium is less likely. In addition, the negative slope of a^*_{Ca} indicates that increasingly more stable compounds $Ca_m X_n$ would be required to prevent boiling as temperature increases.

Open melts of steel could also be refined by introducing calcium as a vapor instead of a compound. The vapor could be introduced directly or formed by slowly introducing metallic calcium which would vaporize rapidly. It would seem desirable to keep the vapor bubbles as fine as possible, to increase the chances of dissolving before being lost to the atmosphere over the melt.

2. Calcium as a Refining Agent in Pressurized Systems

Metallic calcium can be maintained in contact with liquid steel if the pressure of the system exceeds the vapor pressure of the calcium, as in this investigation. Of course some vapor state diffusion can occur, but this is a much slower process than boiling away. If the problem of boiling is eliminated, refining by the calcium takes place for an extended length of time. The process could be enhanced by magnetic stirring of the melt, or by introducing the calcium below the surface of the melt.

In order to observe the refining action of calcium in such a system, two samples of 4340 steel of the following analyses were melted under a calcium layer in the pressure chamber. Melts were held 3 minutes at 2925°F.

COMPOSITION (wt %)

	C	Mn	Cr	Ni	Mo	O_2	S
2054-A	0.42	0.81	0.81	1.98	0.24	0.0135	0.015
2054-B (Vacuum degassed)	.41	0.78	0.81	1.92	0.23	0.0160	0.013

Both samples are from the same heat of steel, but sample 2054-B is from metal which was vacuum degassed before pouring the ingot. The effects of remelting the samples under calcium upon oxygen and sulfur concentrations are of particular interest:

OXYGEN

	Before Calcium Treatment	After Calcium Treatment
2054-A	135 parts per million	3 parts per million
2054-B	160 parts per million	less than 3 parts per million

SULFUR

	Before Calcium Treatment	After Calcium Treatment
2054-A	.015 wt %	.013 wt %
2054-B	.013 wt %	.013 wt %

The oxygen is almost completely removed by the calcium, being reduced from 135 ppm to the limit of analytical error. This reduction is in sharp contrast to the effect of vacuum degassing, after which the reported oxygen concentration is actually higher.

The sulfur content is not affected consistently, with only a moderate reduction in one of the samples. This apparent resistance of the sulfur to being removed by calcium is considered related to the fact that the initial activity of the sulfur in the samples is quite low, since sulfur has essentially unlimited solubility in liquid iron. Therefore the activity of the sulfur corresponding to the initial concentration of sulfur is already quite low, making a further reduction more difficult. Since oxygen on the other hand has very restricted solubility in liquid iron, its initial activity in these samples is relatively high, thus favoring a further reduction in activity by the calcium. It should also be possible to desulfurize better in the presence of a basic slag using calcium, since the calcium sulfide would have a lower activity.

3. Importance of the Immiscibility Between Calcium and Iron

While the lack of extensive solubility of calcium in liquid iron is in some respects disadvantageous from a refining point of view, it does provide, however, a unique advantage over certain conventional refining agents. This advantage is that virtually no calcium should be present in the final product. In contrast to this, deoxidants such as aluminum and silicon are quite soluble in both liquid and solid iron, and therefore the alloying and graphitizing effects of such elements in the solid state must be considered when they are used as refining agents.

4. Significance of the Effects of Alloying Elements upon the Solubility of Calcium in Liquid Iron

Since the five elements of this study have strong effects upon the solubility of calcium in liquid iron, the influence of these changes upon the use of calcium as a refining agent should be considered. Also these influences upon the facility of preparing ferroalloys with large amounts of calcium are discussed.

a. Influence of Alloying Elements in Steel upon the Refining Action of Calcium

The elements which increase the solubility of calcium would be expected to increase its effectiveness as a refining agent. This observation assumes that diffusion of calcium through liquid iron is the rate-controlling step. Higher solubility would permit steeper concentration gradients to be established, resulting in faster diffusion of the calcium in quest of the impurity atoms. Considering the curves of Figure 19 through Figure 23, these elements can be rated according to their expected effectiveness in this regard. The percentage increase in calcium concentration at one weight percent alloying element is used here as a means of estimating the initial effectiveness of an alloying element in promoting the refining action of calcium.

Alloying Element	Change in Calcium Solubility
1 wt% C	90 Pct increase*
1 wt% Si	25 Pct increase
1 wt% Al	20 Pct increase
1 wt% Ni	10 Pct increase

*Extrapolated value

These data show that carbon should be by far the most effective of the four alloying elements on a weight percent basis in enhancing the refining action of calcium. Nickel should be the least effective, with silicon and aluminum falling between the two extremes.

A corollary of the effect just considered is that the tendency to retain calcium in the solid steel would be greatest for alloying elements which increase calcium solubility in liquid iron most strongly. While gold is not commonly added to iron, its effect is quite important inasmuch as it indicates certain types of elements which might have a similar influence upon the solubility of calcium in liquid iron. According to the considerations of section A-2(c), the decrease in calcium solubility upon addition of gold is due to expected positive deviations from ideality for solutions of gold in iron, and negative deviations for solutions of gold in calcium. Copper is expected to lower the solubility of calcium in liquid iron in view of its very strong positive deviations from ideality when dissolved in iron. Copper therefore should sharply reduce the effectiveness of calcium as a refining agent. Other elements having similar deviations from ideality should behave in the same way.

b. Ferroalloys Containing Large Amounts of Calcium

The strong effects exerted by some of the alloying elements upon the solubility of calcium in liquid iron raise the possibility of producing alloys of iron and some other element which contain large amounts of calcium. Such ferroalloys could be used as a means of adding calcium to steel.

Silicon is most interesting in this regard. Ten wt% silicon raises the calcium solubility by an order of magnitude at 2925°F, and if this rate of increase is projected to higher silicon levels, the miscibility gap between calcium and iron should be closed at a silicon concentration of approximately 30 to 40 wt%. Ferrosilicon alloys containing very high concentrations of calcium are therefore possible. This effect is the basis of the present calcium-bearing ferrosilicon alloys. The same possibilities exist for calcium-bearing ferroalloys of aluminum and nickel, although progressively higher levels of aluminum and of nickel should be required to close the miscibility gap between iron and calcium.

C. Theoretical Considerations Regarding the Effects of Third Elements

While the influence of the various alloying elements upon calcium solubility is quite important from an engineering point of view, the theoretical implications of these relations are also of interest. Some theoretical treatments of the effects of third elements have been developed, but these have not been tested extensively, especially for systems such as the present one in which the solute of interest is a metal. The present data may therefore be helpful in the understanding and application of existing theories.

The most prominent theories of interest are those of Alcock and Richardson and of Wagner and these are related to the present data.(14,15)

1. The Alcock and Richardson Equation

From the analysis of a chemical model which considers the energies of old bonds broken and new bonds formed when solute 2 is added to a dilute solution of solute 3 in solvent 1, Alcock and Richardson obtain an equation which may be written as follows for the present study:

$$\left(\frac{\partial(\ln \gamma_{Ca(Fe)})}{\partial N_X}\right)_{N_X \to 0} = \epsilon_{Ca}^{X} = \ln\gamma_{Ca(X)} - \ln\gamma_{Ca(Fe)} - \ln\gamma_{X(Fe)}, \qquad (6)$$

where $\gamma_{Ca(Fe)}$ = activity coefficient of calcium in iron, or in iron-base solutions

N_X = mole fraction of element X,

ϵ_{Ca}^{X} = interaction parameter describing the effect of element X upon the activity coefficient of calcium in iron.

$\gamma_{Ca(X)}$ = activity coefficient of calcium in element X,

$\gamma_{X(Fe)}$ = activity coefficient of element X in iron.

For clarity, the activity coefficient of calcium, rather than the solubility of calcium, is considered in this section, the two terms being uniquely related by the equation

$$N_{Ca(Fe)}\gamma_{Ca(Fe)} = a_{Ca} \cdot \qquad (7)$$

Here $N_{Ca(Fe)}$ is inversely related to the calcium activity coefficient $\gamma_{Ca(Fe)}$. At calcium saturation in the special case of relatively constant activity a_{Ca} an increase in calcium solubility $N_{Ca(Fe)}$ is signified by a decrease in the calcium activity coefficient, $\gamma_{Ca(Fe)}$. For this special case negative values of the interaction parameter ϵ^{X}_{Ca} indicate that additions of element X increase the solubility of calcium in iron. Because the calcium activity may change rather sharply, however, the activity coefficient $\gamma_{Ca(Fe)}$ provides a much better indication of the atomic interactions which occur. While the Alcock and Richardson equation should permit a quantitative prediction of ϵ^{X}_{Ca}, this is only possible when data are available for each of the three activity coefficients on the right-hand side of Equation (6). The second term, $-\ln\gamma_{Ca(Fe)}$, for this study is - 7.7, the third term, $-\ln\gamma_{X(Fe)}$, is 0.0 for nickel, 0.5 for carbon, 3.1 for aluminum, and 4.0 for silicon.(22,24) No data are available for gold. Furthermore, no data are available for the first term, $\ln\gamma_{Ca(X)}$, for any of the alloying elements. In the unlikely event that this term should have a rather high positive value, it is evident that the second term would still predominate, leading to negative interaction parameters for all of the present alloying elements.

a. Determination of Interaction Parameters

The interaction parameters for the present data may be determined from Equation (7). The value of $N_{Ca(Fe)}$ is the analyzed calcium concentration in the iron, expressed as an atom fraction. The limiting reasonable values of a_{Ca} are considered here for the various alloying elements in the absence of activity data for these elements in the calcium-rich layer. Aluminum, silicon and carbon are expected to dissolve preferentially in iron in view of the negative deviations from ideality for these elements in iron. Furthermore, nickel, which forms ideal solutions with iron, can be shown to favor solution in the iron layer slightly by a mass balance. Thus the concentration of alloying element in the calcium-rich layer should not exceed that in the iron-rich layer, this limiting value representing a 1:1 partition of alloying element between the two layers. Assuming Raoult's law for the activity of calcium in the calcium-rich layer, this establishes the lower limit of calcium activity as $1-N_{X(Fe)}$. The lower limit of alloy concentration in the calcium-rich layer is zero, for which the upper limit of calcium activity is unity. Thus when the iron contains 2 at % aluminum, for example, the calcium activity should be between 0.98 and 1.00. At 5 at % aluminum, the range would be 0.95 to 1.00; at 10 at % aluminum, 0.90 to 1.00; and at 20 at % aluminum, 0.80 to 1.00. The range of uncertainty regarding calcium activity is seen to be quite small at low aluminum levels, increasing as the aluminum concentration of the iron increases.

The actual determination of interaction parameters may be followed in Table III for the case of an equal molar concentration of the alloying element in both liquids. The activity of the calcium, a_{Ca}, is taken as the mole fraction of calcium in the calcium-rich liquid, which for the 1:1 partition of X considered here equals $(1-N_{X(Fe)})$. From this the activity coefficient of calcium in the iron-rich layer is determined by the relationship

$$\gamma_{Ca(Fe)} = \frac{a_{Ca}}{N_{Ca(Fe)}} . \qquad (8)$$

Substituting,

$$\gamma_{Ca(Fe)} = \frac{1-N_{X(Fe)}}{N_{Ca(Fe)}} . \qquad (9)$$

Activity coefficients of calcium are seen to range from an average of 2270 for calcium in pure iron to 178 for calcium in iron containing 19.02 At.% (10.5 Wt.%) silicon. The natural logarithm of $\gamma_{Ca(Fe)}$ is plotted against $N_{X(Fe)}$ in Figure 25, and the interaction parameter for this 1:1 partition termed $(\epsilon^X_{Ca})_{1:1}$ is the limiting slope as $N_X \longrightarrow 0$. Values of $(\epsilon^X_{Ca})_{1:1}$ are listed in Table III.

The dashed curve of Figure 25 represents $\ln\gamma_{Ca(Fe)}$ for $a_{Ca(Fe)} = 1$, the value assuming that none of the alloying element enters the calcium-rich layer. The limiting slope for this condition is represented by $(\epsilon^X_{Ca})_{0:1}$, and may be shown analytically to be 1 greater than that for the condition of a 1:1 partition. Thus,

$$(\epsilon^X_{Ca})_{0:1} = (\epsilon^X_{Ca})_{1:1} + 1, \qquad (10)$$

TABLE III

DETERMINATION OF INTERACTION PARAMETER ϵ^{X}_{Ca}

Heat Number	$(N_{Ca(Fe)})10^2$	$(N_{X(Fe)})10^2$	$a_{Ca}=(1-N_{X(Fe)})$	$\gamma_{Ca(Fe)}=\frac{a_{Ca}}{N_{Ca(Fe)}}$	$\ln\gamma_{Ca(Fe)}$	$(\epsilon^{X}_{Ca})_{1:1}$ (from Fig.25)	$(\epsilon^{X}_{Ca})_{0:1}$ $[=(\epsilon^{X}_{Ca})_{1:1}+1]$,	ϵ^{X}_{Ca}(Range)
Pure Iron								
99	0.045	----	1.0000	2220	7.706			
100	0.043	----	1.0000	2320	7.750			
Aluminum Series						-8.0	-7.0	-7.0 to -8.0
125	0.056	2.19	0.9781	1750	7.469			
126	0.070	5.41	0.9459	1350	7.208			
127	0.083	9.81	0.9019	1090	6.994			
128	0.185	19.72	0.8028	434	6.073			
Carbon Series						-16.3	-15.3	-15.3 to -16.3
122	0.061	1.70	0.9830	1610	7.386			
123	0.070	3.35	0.9665	1380	7.231			
Nickel Series						-11.2	-10.2	-10.2 to -11.2
115	0.057	2.03	0.9797	1720	7.453			
112	0.072	4.90	0.9410	1310	7.178			
113	0.115	9.90	0.9010	783	6.663			
114	0.292	18.97	0.8103	278	5.627			
Silicon Series						-11.2	-10.2	-10.2 to -11.2
107	0.051	2.19	0.9781	1920	7.561			
104	0.081	5.02	0.9498	1170	7.066			
105	0.118	9.79	0.9021	764	6.639			
106	0.456	19.02	0.8098	178	5.182			

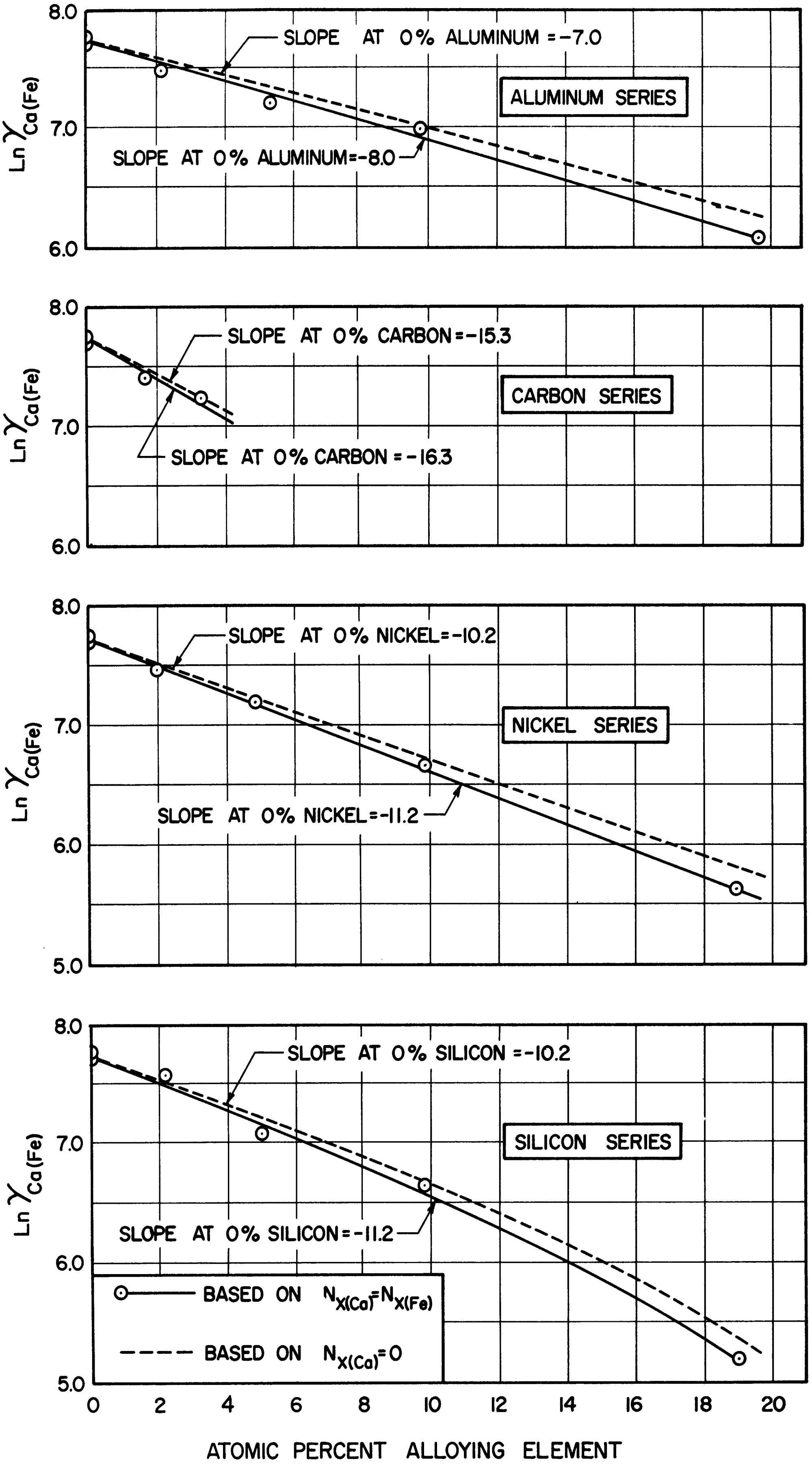

Figure 25. Effect of Alloying Element Concentration in the Iron-Rich Liquid Upon the Activity Coefficient of Calcium in the Iron-Rich Liquid at 2925°F.

The value of $(\epsilon^{X}_{Ca})_{0:1}$ for aluminum, for example, is determined by

$$
\begin{aligned}
(\epsilon^{Al}_{Ca})_{0:1} &= (\epsilon^{Al}_{Ca})_{1:1} + 1 \\
&= -8.0 + 1 \\
&= -7.0
\end{aligned}
$$

Values of $(\epsilon^{X}_{Ca})_{0:1}$ are included in Table III, and the range of values for the two terms is listed here:

Alloying Element	ϵ^{X}_{Ca} (Range) $(\epsilon^{X}_{Ca})_{0:1}$	to	$(\epsilon^{X}_{Ca})_{1:1}$
Al	- 7.0	to	- 8.0
Ni	-10.2	to	-11.2
Si	-10.2	to	-11.2
C	-15.3	to	-16.3

From this, the range of ϵ^{X}_{Ca} due to the uncertainty of calcium activity is relatively small, and does not greatly influence the rank of the alloying elements.

The heats containing gold do not lend themselves to this evaluation of the interaction parameter. This is so because the extremely high concentration of gold in the calcium layer prevents the making of a reasonable estimate of the calcium activity in this layer.

b. Direct Application of the Alcock and Richardson Equation

Considering the values ϵ^{X}_{Ca} in the light of the Alcock and Richardson equation, the prediction of negative values of ϵ^{X}_{Ca} is verified for the elements considered here, aluminum, carbon, nickel and silicon. Theoretical values of ϵ^{X}_{Ca} cannot be calculated for purposes of comparison with the experimental values, however, because of lack of data for $\gamma_{Ca(X)}$.

c. Qualitative Consideration of the Alcock and Richardson Equation

If the terms on the right hand side of Equation (6) are considered individually, it is seen that this equation may be interpreted in terms of atomistic effects between the different species. In this regard, a small activity coefficient (less than 1) is considered indicative of an attraction between the two different atoms, while a large activity coefficient (greater than 1) is considered related to a repulsion between the two atoms.

Considering the second term $(-\ln\gamma_{Ca(Fe)})$, which predominates in this equation because of the immiscibility in the iron-calcium system, this term very strongly favors negative values for ϵ_{Ca}^{X}. Atomistically, this means that iron and calcium atoms have strong repulsions for each other, making it very easy, therefore, for element X to exhibit its attraction for calcium. Qualitatively then, most elements are expected to lower the activity coefficient of calcium in iron, resulting in negative values for X, as with the four elements considered here.

Since the second term of Equation (6) is the same for all alloying elements, attention may be focused on the remaining two terms, $(\ln\gamma_{Ca(X)})$ and $(-\ln\gamma_{X(Fe)})$, in an effort to understand how one element might be more effective than another in changing the activity coefficient of calcium in iron. A negative interaction parameter is favored by negative values of $\ln\gamma_{Ca(X)}$, indicative of an attraction between calcium and X, and by positive values of $\ln\gamma_{X(Fe)}$, indicative of a repulsion between iron and X. Atomistically, this means that if X has a greater attraction for calcium atoms than for iron atoms, a negative value of ϵ_{Ca}^{X} is favored.

Two different alloying elements may be compared on this basis, regarding their effect on the interaction parameter ϵ_{Ca}^{X}, by the following criterion. The element which has the greater attraction for calcium atoms as compared to its attraction for iron atoms should result in the more negative value of ϵ_{Ca}^{X}. Thus it should be possible to estimate which of two elements would cause the more negative value of ϵ_{Ca}^{X}, if information concerning the attraction of these two elements for calcium and for iron is available. One reasonable index of the attraction between atoms is the standard free energy of formation of a compound formed by the two atoms at the temperature of the study, 2925°F. Of the alloying elements considered here, data are available only for carbon.(21) For the other elements, one index which suggests itself is to compare the number of intermetallic compounds in the system X-Fe with that in the system X-Ca.

An evaluation of the relative magnitude of the attractions X-Ca and X-Fe is presented in Table IV, with the alloying elements arranged in order of increasing negative values of ϵ_{Ca}^{X} (progressively greater reductions in the activity coefficient of calcium $\gamma_{Ca(Fe)}$).(6)

Table IV shows that there is some relation between this criterion of atom preference and the interaction parameter ϵ_{Ca}^{X}. While it would be unreasonable to expect this criterion to correlate exactly with the values of ϵ_{Ca}^{X}, it does seem significant that aluminum, which reduces $\gamma_{Ca(Fe)}$ the least, indicates a preferential attraction for iron atoms, while carbon, which reduces $\gamma_{Ca(Fe)}$ the most, indicates a preferential attraction for calcium atoms.

In the absence of suitable activity data, the criteria of free energy of compound formation, or of the number of intermetallic compounds

TABLE IV

RELATION OF ATOMISTIC PREFERENCE OF ELEMENT X TO OBSERVED INTERACTION PARAMETER ϵ_{Ca}^{X}

Alloying Element X	Compound formation in the system X-Ca(6)	Compound formation in the system X-Fe(6)	Indicated preference of X atoms	ϵ_{Ca}^{X} (Range)
Al	2 compounds	4 compounds	Preference for Fe Atoms	-7.0 to -8.0
Ni	1 compound	0 compounds	Preference for Ca Atoms	-10.2 to -11.2
Si	3 compounds	3 compounds	Indefinite	-10.2 to -11.2
C	$\Delta F_f^\circ = -12,800$* for 1/2 CaC_2 at 2925°F.(21)	$\Delta F_f^\circ = -1,600$ for Fe_3C at 2925°F.(21)	Preference for Ca Atoms	-15.3 to -16.3

---

* Reference of Ca taken as liquid state.

formed, may serve as a useful guide in assessing which of several elements will change most sharply the activity coefficient of a solute species.

2. Wagner's Electron-to-Atom-Ratio Concept

The application of Wagner's theory requires a knowledge of the number of free electrons which an atom possesses in a metallic solution. As a first approach to the problem (following Wagner) the number of valence electrons may be used to represent this number.

a. Correlation of the Data With Chemical Valence

The interaction parameters from the previous section may be now compared with the chemical valence for each element in question:

Element	Chemical Valence	ϵ_{Ca}^{X} (Range)
Ca	2	
Fe	2,3	
Al	3	-7.0 to -8.0
Ni	2,3	-10.2 to -11.2
Si	4	-10.2 to -11.2
C	4	-15.3 to -16.3

If the valence numbers are applied directly to the Wagner model, two cases need to be considered, in view of the two possible valences for iron. If iron is considered first in the plus 2 valence state, it has the same number of free electrons as calcium, and therefore it is not possible that the number of free electrons of alloying element X and of calcium could differ in opposite directions from that for iron. One possible interpretation of the Wagner theory for a situation of this type is that if the valence of X were the same as for iron and calcium, then the electron chemical potential would not change, and the activity coefficient of the calcium would remain the same, corresponding to a value of zero for ϵ^{X}_{Ca}. For any third element having a lower or higher valence than that of calcium and iron, the chemical potential of the electrons would change, and an increase in activity coefficient of the calcium is indicated. This would result in a positive value of the interaction parameter, ϵ^{X}_{Ca}. The experimental values do not support either of these predictions.

If the plus 3 valence state of iron is considered, then nickel for the plus 2 state should give a positive value of ϵ^{X}_{Ca}, aluminum and nickel in the plus 3 state should result in a value of zero for ϵ^{X}_{Ca}. While these values agree to some extent with the experimental data, the level of agreement is poor.

The use of valence as a guide to the number of free electrons is a rather unsatisfactory index for most elements, and one which Wagner avoids when other means are available. The chemical valence can be a very misleading guide to the number of free electrons contributed to the bulk metal by an element. Silicon, with a valence of plus 4, might be expected to contribute more free electrons than calcium, with a valence of plus 2. The very low electrical conductivity of metallic silicon relative to that of calcium, however, refutes this possibility. Furthermore, the use of chemical valence would indicate that all elements with the same valence should contribute free electrons to a metallic solution with equal facility in spite of differences in electron structure between atoms. Still other objections to the use of valence as a means of interpreting the Wagner theory can be raised.

b. Alternate Criteria for Assessing the Number of Free Electrons

Various other characteristics of an element may be considered as an index of how readily an element gives up electrons when it dissolves in a metallic solution. One index of interest is electronegativity, which Pauling defines as the power of an atom in a molecule to attract electrons to itself.(25) By this definition, an atom of high electronegativity such as carbon might be expected to contribute fewer free electrons than an element such as calcium of low electronegativity. While the absolute value of electronegativity may not be meaningful here, the relative values for the various elements may provide a useful index of the number of free electrons contributed by an atom.

In Table V electronegativity values are listed for calcium, iron and the alloying elements, along with the interaction parameters ϵ_{Ca}^{X}. The values of electronegativity are those for the model of Pauling based on bond energies.(26) Considering the electronegativity calculated for the plus 2 state of iron, the theory of Wagner suggests that ϵ_{Ca}^{X} be positive for aluminum and negative for nickel, silicon and carbon. All of the elements except aluminum conform to the theory, using Pauling's electronegativity as an index of the contribution of free electrons. Furthermore, the interaction parameters are seen to become more negative in approximate order of increasing electronegativity. For the present data, electronegativities permit a reasonably good qualitative and quantitative correlation with the theory of Wagner.

The other possible indexes of the number of free electrons which an element contributes in a metallic solution, the ionization potential and the photoelectric work function, may also be considered.

TABLE V

ALTERNATE CRITERIA FOR APPLYING WAGNER'S ELECTRON THEORY

Element	ϵ^{X}_{Ca} (Range)	Electronegativity		1st Ionization Potential		Photoelectric Work Function	
		Pauling's E.N.	Predicted sign of ϵ^{X}_{Ca}*	Value in Electron Volts	Predicted sign of ϵ^{X}_{Ca}	Value in Electron Volts**	Predicted sign of ϵ^{X}_{Ca}
Ca	----	1.0		6.11		2.86	
Fe	----	Fe^{II} 1.65 (Fe^{III} 1.80)		7.90		4.47	
Al	-7.0 to -8.0	1.5	(+)	5.98	(+)	3.80	(+)
Ni	-10.2 to -11.2	1.7	(-)	7.63	(+)	4.61	(-)
Si	-10.2 to -11.2	1.8	(-)	8.15	(-)	4.52	(-)
C	-15.3 to -16.3	2.5	(-)	11.26	(-)	4.81	(-)

* Based on Fe^{II} .

** Average of all listed values for each element.

The first ionization potential, which is the energy required to remove an electron from a neutral free atom, is listed in Table V for each element.(27) Considering the ionization potentials in the light of Wagner's theory, positive values of ϵ^{X}_{Ca} are predicted for aluminum and nickel, and negative values for silicon and carbon. Silicon and carbon corroborate the Wagner theory using ionization potential as an index as to the contribution of free electrons. As with electronegativity, the values of ionization potential change rather regularly with the observed interaction parameters.

Finally, photoelectric work function may be considered as a guide to the contribution of free electrons by an element. The photoelectric work function is the energy a photon must have in order to remove an electron from an element, ordinarily measured for the solid state. Average values of the photoelectric work function are listed in Table V.(28) The signs of the interaction parameters for all the elements except aluminum corroborate the theory of Wagner on this basis, and again the values of the interaction parameters are in approximate order of increasing values of the work function.

In summary, three separate guides as to the contribution of free electrons by an element dissolved in metallic solution are considered as a means of applying the qualitative theory of Wagner. In eight of twelve instances, the sign of the predicted interaction parameter agrees with that of the experimental value. Furthermore, experimental values of the interaction parameters change in an essentially regular manner with changes in each of the indexes considered. This suggests the possible use of these indexes as a guide in predicting which of two elements will have the greater effect in changing the activity coefficient of an element in metallic solution.

c. The Wagner Equation for the Electron-to-Atom-Ratio Concept

The equation derived by Wagner for the electron model of metallic solutions may be written

$$\epsilon^{X}_{Ca} = \epsilon^{Ca}_{X} = \pm \left(\epsilon^{Ca}_{Ca} \, \epsilon^{X}_{X} \right)^{1/2}_{N_{Ca} \rightarrow 0,\ N_X \rightarrow 0} . \qquad (11)$$

In attempting to apply this equation to the present work, a serious problem arises. The self-interaction parameter ϵ^{Ca}_{Ca}, which represents the initial change in the activity coefficient of calcium in iron according to the relationship $\frac{\partial \ln \gamma_{Ca(Fe)}}{\partial N_{Ca}}$, is expected to be negative for this immiscible system. Such behavior is observed for the immiscibility between zinc and lead, for example.(29) At the same time, the term ϵ^{X}_{X} for aluminum, silicon and carbon in iron is positive, leading to imaginary values of ϵ^{X}_{Ca}, which have no meaning. For the alloying element nickel, which exhibits ideal behavior in liquid iron, the term ϵ^{Ni}_{Ni} is essentially zero, leading to a value of zero for ϵ^{Ni}_{Ca}. This is quite inconsistent with the observed interaction parameter for nickel.

From the foregoing, the quantitative relationship of Wagner does not lend itself to an analysis of the present data.

3. Summary of the Present Data in Relation to Theory

The chemical model of Alcock and Richardson and the electron model of Wagner have been considered in the light of the present data.

The former model correctly predicts negative values of the interaction parameters, and permits the alloying elements to be arranged in approximate order of increasing magnitude of this parameter by the use of a suggested criterion. The latter model, applied by means of several suggested criteria, is somewhat less successful in predicting the negative values of interaction parameter observed. By these criteria, however, the relative effects of various elements upon the activity of calcium are rather accurately predicted.

Thus both theories provide reasonable agreement with the experimental data, in spite of differences in the theoretical models. The model of Alcock and Richardson considers interactions between the various pairs of atoms. Electron effects are not considered directly, although they presumably are reflected in the bond energies involved in this analysis. The electron model presented by Wagner takes into account the relative number of free electrons contributed by solvent and solute atoms, but does not allow for interaction effects between positive metal ions.

In view of the reasonably good agreement between both theoretical models and the present experimental data, it would seem that the contributing of free electrons cannot be completely divorced from any interactions between the positive metal ions which contributed the electrons. The studies of Alcock and Richardson and Wagner are, therefore, distinct but reasonably compatible approaches to the same problem.

CONCLUSIONS

On the basis of the present investigation, the following conclusions may be drawn:

1. Calcium has significant solubility, 0.032 Wt. %, in liquid iron at 2925°F. The corresponding thermodynamic activity coefficient for calcium in liquid iron is 2270.
2. The solubility of calcium in liquid iron is strongly affected by the alloying elements studied.
3. The solubility effects observed have important implications in the field of ferrous process metallurgy.
4. The effects of alloying elements agree reasonably well with current theories. Criteria are suggested to facilitate the application of these theories to studies of this type.
5. A sampling technique and crucible material have been developed which facilitate future investigations of reactive metals of high vapor pressure.

Many topics for future study are suggested by the present research. Profitable areas of future work in systems of this type might include the following: the additivity of the effects of alloying elements; the effects of alloying elements at the extreme ends of the scales of electronegativity, ionization potential, or work function; the concentrations of alloying elements required to close the miscibility gap; and the solid solubility of calcium and other immiscible elements in ternary alloys of iron.

APPENDIX I

CRUCIBLE MATERIALS

1. Evaluation of Existing Refractories

Pieces from the best crucibles commercially available were exposed to molten lithium for approximately 10 minutes at 2500°F. Because lithium is more active chemically than calcium, this was considered to be an indication of the ability of a crucible to withstand attack by molten calcium at the higher temperatures of the present study. Tests were conducted by placing a small piece of the crucible to be tested, 1/16 in. to 1/8 in. in thickness, along with a piece of lithium, in a hollow iron bomb-type container, and inserting a tapered iron plug. This was done inside a glove box, and the plug was subsequently arc-welded shut. These containers were then heated to 2500°F in an induction furnace.

The materials tested were as follows:

TAM ZrO_2

Norton MgO, mix M 204

Magnafrax 0340 high purity MgO

Triangle RR Al_2O_3

Thoria-Lined Triangle RR Al_2O_3

Leco ThO_2

Synthetic sapphire single crystal

Silicon nitride, experimental grade

Boron nitride

The level of performance of all materials was unsatisfactory, with the pieces being converted into a darkened and softened mass. Pieces of the titanium nitride material developed in this investigation were unaffected by lithium in these tests.

In addition, crucibles of hafnium carbide backed up by tungsten, produced by plasma spraying, were considered for this study. However the experimental crucible of this type failed by thermal shock when iron was melted in it.

2. Typical Data for a Set of Crucibles

Compacted crucibles are sintered in groups of five, and are subsequently nitrided in larger groups. The data for the five crucibles sintered in Heat C-42 are presented in Table I, and characteristics are seen to be rather uniform. The drop in water level is reasonably low, approximately 3/32 in. in 1 hour. Linear shrinkage is seen to average 13.1 percent and sintered densities average 4.48 gm/cm^3.

During the nitriding treatment which follows sintering, the crucibles gained approximately 5 percent in weight, attaining an average density of 4.65 gm/cm^3. This corresponds to 86 percent of the theoretical density of 5.43 gm/cm^3 for titanium nitride of stoichiometric composition.(19)

APPENDIX I

TABLE I

CHARACTERISTICS OF CRUCIBLES FROM SINTERING HEAT C-42

Crucible No.	Drop in Water level after 1 hr. (In.)	Linear Shrinkage (Pct.)	Density after Sintering (gm/cm^3)	Weight gain during Nitriding	Density after Nitriding (gm/cm^3)
158	3/32	13.2	4.48	5.1%	4.65
160	1/16	13.3	4.48	5.0%	4.65
161	3/32	12.7	4.48	5.1%	4.65
162	3/32	13.1	4.49	4.7%	4.66
163	3/32	13.1	4.48	4.8%	4.65
Average	3/32	13.1	4.48	4.9%	4.65

APPENDIX II

CHEMICAL ANALYSIS

In this section the chemical analysis procedure for calcium is considered in detail. The determination of calcium in unalloyed samples is considered first, followed by sections for the analysis of alloyed samples.

A. Determination of Calcium in Unalloyed Samples

The unalloyed samples contain approximately 0.25% titanium picked up from the titanium nitride crucible, and trace amounts of nickel, silicon, copper, chromium and other elements, in addition to calcium. The key steps in the basic procedure are carefully considered here, as well as the reproducibility for this procedure, and the actual step-by-step procedure employed.

1. Basic Operations for Unalloyed Samples

a. Dissolving of samples. The 1.5 gm iron samples are dissolved in aqua regia. This permits samples to be dissolved in less than 30 minutes as contrasted to 8 to 12 hours required to dissolve the samples in diluted hydrochloric acid. Samples are taken to dryness to expel the nitric acid.

b. Removal of iron. Morrison and Freiser recommend extracting iron as the ferric ion from a 7.75-8.0 M hydrochloric acid solution with isopropyl ether.(30) Accordingly, the iron is oxidized with 30% hydrogen peroxide and then extracted with isopropyl ether in a solution containing 2 parts hydrochloric acid to 1 part water. It is possible to extract at least 99.95 percent of the iron in a double extraction by insuring that the iron is fully oxidized.

c. Removal of titanium and trace iron. The organic reagent cupferron is capable of quantitatively precipitating titanium, ferric iron, and other metals from solution.(31) Because the action is less specific at low acidity, the acidity is purposely reduced to approximately 2% hydrochloric acid for this operation.

The precipitation is conducted in the presence of diethyl ether, with the precipitate dissolving entirely in the ether. This avoids the danger of losing calcium on the precipitate, and is possible because calcium chloride is insoluble in diethyl ether. No trace of iron or titanium remains after this step.

d. Determination of calcium. Versene is commonly used in a titration to measure relatively high calcium concentrations. The exhaustive study of Schwarzenbach was found extremely useful in adapting the use of versene to the present determinations of trace levels of calcium.(32)

A dilute versene solution, 0.001 M, permits accurate titrations with a 50 ml burette. Solutions are adjusted to a pH of 10.5 with a buffer solution. Approximately 0.05 Mg of magnesium is added as magnesium versenate to sharpen the endpoint. It is necessary to mask the trace nickel, chromium and any other interfering elements with sodium cyanide to permit the observation of the endpoint. Two aliquots of each solution are titrated.

A concentration series was titrated and found to give exact linearity between the volume of versene and the amount of calcium taken, even at the low concentrations of this study.

2. Reproducibility for Unalloyed Samples

Five synthetic unknowns containing 0.0467% calcium were prepared and analyzed for the purpose of assessing the accuracy of the method for unalloyed samples. The percentage deviations of analyzed calcium from the mean for the group are listed:

Solution Number	Percentage deviation from mean
264	+ 4.70%
265	- 3.27%
266	- 3.42%
267	- 1.85%
268	+ 3.80%

The standard deviation σ for this set is 3.96% of the amount analyzed, or 0.00184% calcium.

3. Standard Procedure (for Analyzing Unalloyed Samples)

Stock Solutions:

1. 100 ppm calcium standard. Prepared by dilution from a 952 ppm calcium standard which was analyzed by a standard calcium oxalate precipitation (triplicates analyzed). The standard calcium solutions have an HCl concentration of 1%.
2. 2000 ppm titanium solution. Sponge titanium dissolved in 25% HCl.
3. 2/1 HCl solution. Two parts concentrated hydrochloric acid to one part demineralized H_2O.

4. 1% HCl solution. One part concentrated hydrochloric acid to 99 parts demineralized H_2O.

5. H_2O. All H_2O employed in this study is demineralized, obtained by passing distilled H_2O through a "Deeminac" ion exchange resin cartridge.
6. 5% Cupferron solution. Five gm cupferron dissolved in 100 ml H_2O, freshly prepared.
7. pH 10.5 buffer. $NH_4OH/NHCl$ solution, adjusted to pH 10.5 on pH meter.

Procedure:

1. Prepare blank by adding 2.25 ml of 2000 ppm Ti solution to 1.5 gm Ferrovac 'E' iron.
2. Prepare 0.0667% Ca standards by adding 10 ml of 100 ppm Ca standard and 2.25 ml of 2000 ppm Ti solution to 1.5 gm Ferrovac 'E' iron.
3. Dissolve blank, standards and unknowns in 10 ml conc. HCl and 5 ml HNO_3, in 150 ml beakers with watch glasses. Heat to initiate reaction.
4. Raise watch glasses on glass hooks, evaporate without boiling carefully to dryness to expel nitric acid fumes.
5. Cool, remove glass hooks, and drench with 2/1 HCl. Heat to redissolve salts.
6. Cool, add 3 ml 30% H_2O_2, simmer 30 minutes. Remove from heat, add 3 drops 30% H_2O_2.
7. When cool, dilute to 50 ml in 600 ml separatory funnel. Extract with 200 ml isopropyl ether. Rinse with 5 ml 2/1 HCl. Re-extract with 100 ml isopropyl ether. Rinse with 5 ml 2/1 HCl.

8. Evaporate solution to 5 ± 1 ml without boiling, using watch glasses and glass hooks. Add 10 ml H_2O, 1 ml 30% H_2O_2, evaporate solution to 5 ± 1 ml. without boiling.
9. Dilute with 1% HCl to 30 ml in separatory funnel. Add 100 ml diethyl ether. Add cupferron batchwise until yellow titanium precipitate stops forming. Shake until solution clears. Rinse with 5 ml 1% HCl. Re-extract using 1 ml 5% cupferron solution and 100 ml diethyl ether, and rinse with 5 ml 1% HCl.
10. Evaporate to 20 ml without boiling, using watch glasses and glass hooks, filter through Whatman's No. 41 paper, 11 cm, to 50 ml in volumetric flask.
11. Titrate each of two 20 ml aliquots as follows. Add 1 drop methyl red indicator. Adjust with dilute NaOH solution to give pH 10.5 on pH 10-12 paper. Add 20 ml pH 10.5 buffer. Add 10 drops 0.01M magnesium versenate solution, 1 ml 2% NaCN solution, 6 drops eriochrome black T indicator. Titrate to disappearance of last trace of red.

B. Determination of Calcium in Alloyed Samples

The basic procedure of the previous section can be readily adapted to samples which contain aluminum, carbon, gold, nickel and silicon.

1. Iron Samples Containing Aluminum.

While aluminum is ordinarily rather difficult to remove from solution, it can be removed quantitatively from the present solutions with cupferron, according to the method of Welcher, when the solution has a pH between 2.5 and 4.5.(31) The precipitation is not complete at lower pH and at a higher pH the gelatinous aluminum hydroxide precipitate forms. Aluminum is removed following the standard cupferron extraction. The aluminum precipitate is soluble in diethyl ether, permitting it to be extracted with this phase.

Procedure for samples containing aluminum:

1. Steps 1 through 9 of standard procedure, adding 2, 10 and 20 at% aluminum as metallic aluminum to the standards of Step 2.

2. Adjust solution to pH 3 by adding concentrated NaOH dropwise. Transfer into 600 ml separatory funnel, add 200 ml diethyl ether, add 5% cupferron batchwise until white precipitate stops forming. Rinse with 5 ml H_2O. Readjust pH to 3, add 100 ml diethyl ether. Add 5% cupferron batchwise until white precipitate stops forming. Rinse with 5 ml H_2O, re-extract with 100 ml diethyl ether and 1 ml 5% cupferron.
3. Steps 10 and 11 of standard procedure.

2. Iron Samples Containing Carbon.

Carbon causes little change in the standard procedure. Any carbon residue is removed by filtration prior to the isopropyl ether extraction.

Procedure for samples containing carbon:

1. Steps 1 through 6 of standard procedure, adding 2 and 10 at % carbon as carbon-saturated iron to the standards of Step 2.
2. Filter through Whatman's No. 41 11-cm paper into separatory funnel, add 3 drops 30% H_2O_2, extract according to Step 7 of standard procedure.

3. Steps 8 through 11 of standard procedure.

3. Iron Samples Containing Gold

The presence of gold in iron causes no difficulty in the procedure for determining calcium. Gold is extracted by isopropyl ether simultaneously with the iron, both as trivalent chlorides.(33) Gold is subsequently precipitated with ferrous sulfate from aqueous solution and determined gravimetrically.(33)

Procedure for samples containing gold:

1. Steps 1 through 6 of standard procedure, adding 2 and 10 at % gold to the standards of Step 2 as chlorauric acid, $HAuCl_4 \cdot 3H_2O$.
2. Step 7 of the standard procedure, saving the isopropyl ether for the subsequent determination of gold.
3. Steps 8 through 11 of standard procedure.

4. Iron Samples Containing Nickel

Nickel is not removed by an isopropyl ether extraction or by cupferron, therefore requiring a special step in the procedure. The nickel is electrolytically deposited from an ammoniacal solution following the cupferron extraction, according to the method described by Kolthoff and Sandell.(34) This method involves the addition of a small amount of concentrated sulphuric acid to accelerate the deposition of nickel by increasing the conductivity of the solution. (The increase in weight of the platinum gauze electrode serves to determine the nickel in the sample.)

Procedure for samples containing nickel:

1. Steps 1 through 9 of the standard procedure, adding 2, 10 and 20 at% nickel as a high-purity nickel chloride solution in Step 2.
2. Evaporate to 20 ml without boiling, using watch glasses with glass hooks.

3. Transfer to a 250 ml electrolyzing beaker. Add 3 ml H_2SO_4, 20 ml NH_4OH, dilute to 100 ml with H_2O. Electrolyze at 6 volts for 40 minutes, using a platinum gauze cathode and platinum wire anode.
4. Steps 10 and 11 of standard procedure adjusting pH to 10.5 with the aid of a pH meter before adding the buffer in Step 11.

5. Iron Samples Containing Silicon

The presence of silicon requires very special handling of solutions. This is because the bulk of the silicon must be removed by a precipitation, requiring careful technique to minimize the loss of the calcium species with the precipitate, and because sufficient hydrated silica remains in solution even after four precipitations to obscure the endpoint during titration.

Silica is removed by separate filtrations before and after the isopropyl ether extraction. Solutions are dehydrated without excessive baking, and the precipitate rinsed with hot 2/1 HCl during filtering, all according to the best techniques described by Kolthoff and Sandell, in order to minimize any calcium loss.

The calcium is freed from the hydrated silica remaining in solution by collecting the calcium on a cation exchange resin, while the silica passes on through and is discarded. The calcium is subsequently removed from the column and finally analyzed. Calcium is deposited on the column at 1% HCl acidity, and is removed from the column with 2/1 HCl and concentrated HCl, following the method of Campbell and Kenner.(35) The procedure employed for the ion exchange technique is the result of studies of column heights, flow rates, acidity levels and rinsing procedures, with calcium concentrations being measured at all stages of the study with a Beckman flame spectrophotometer.

Procedure for samples containing silicon:

1. Step 1 of standard procedure.
2. Prepare 0.0667% Ca standards by adding 10 ml of 100 ppm Ca standard and 2.25 ml of 2000 ppm Ti solution and 2, 10 and 20 at % silicon as a vacuum-melted iron alloy containing 12 wt% silicon.
3. Dissolve samples in a total of 65 ml HCl, 40 ml HNO_3, 20 ml H_2O, with watch glasses, without boiling. (Approximately 30 hours required for dissolution.)
4. Step 4 of standard procedure.
5. Cool and drench with 5 ml 2/1 HCl for 3 minutes. Dilute to 30 ml with 1% HCl. Simmer for 5 minutes. Cool, filter through Whatman's No. 41 11-cm paper with 10 ml hot 2/1 HCl, followed by 1% HCl.
6. Evaporate solution to 10 ml without boiling, using watch glasses and glass hooks, cool and dilute to 30 ml with 2/1 HCl.
7. Steps 6 and 7 of standard procedure.
8. Evaporate without boiling or spattering just to dryness, using watch glasses and glass hooks. Hold for 30 minutes in an oven at 110 °C.
9. Repeat Step 5.
10. Steps 8 and 9 of standard procedure substituting H_2O for 1% HCl.
11. Heat 10 minutes, with watch glasses, to expel ether.

12. Prepare resin column by filling with Dowex 50 resin, previously washed thoroughly in 2/1 HCl, into a 50 ml burette to a height of 3.5 cm. Rinse column with 150 ml HCl at 8 ± 2 ml per minute.

13. Dilute the sample solution to 75 ml with 1% HCl, pass through column and rinse with three 10 ml-portions of 1% HCl at 3 ± 1 ml per minute. Collect this solution and test for calcium in a flame photomoter. (All solutions showed a negligible amount of calcium here.)

14. Rinse the column with 300 ml 1% HCl at 8 ± 2 ml per minute, and test this solution for calcium in a flame photometer. (All solutions showed a negligible amount of calcium here.)

15. Collect the calcium from the column with 75 ml 2/1 HCl and 50 ml Conc. HCl at 3 ± 1 ml per minute. Prepare column for subsequent samples by rinsing with 200 ml H_2O at 8 ± 2 ml per minute.

16. Steps 10 and 11 of standard procedure.

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