

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

REPORT OF A LITERATURE SURVEY
OF
HIGH-TEMPERATURE METALLURGICAL REFINING PROCESSES

by

J. G. Lewis
R. J. Annesser
R. J. Hennig
Marx Weech

H. A. Ohlgren, Project Advisor

IP-105

February, 1955

We wish to express our appreciation
to the Detroit Edison Company for
permission to issue this report
under the College of Engineering
Industry Program.

PREFACE

This report is presented as a record of a literature search on the subject of high temperature metallurgical refining processes. The search was conducted as a part of research Project No. 2300, administered by the Engineering Research Institute of the University of Michigan and supported by the Consumers Power Company of Jackson, Michigan for the Dow Chemical-Detroit Edison and Associates Atomic Power Development Project.

The body of the report consists of selected abstracts from the post-World War II literature of the metals industry. The material abstracted is not advanced as a complete documentary of current metals refining practice and research, but only as a preliminary compilation of some representative recent literature.

Because literature on refining and related metallurgical processes is so great in volume, it was impossible to review more than a segment of the total. A preliminary title search was conducted and several hundred titles and extremely brief abstracts were collected. From this collection were selected the sixty papers which are cited below. The selection was admittedly somewhat arbitrary, but was made with the best knowledge available at the time and was amended as the work progressed. A supplementary list of references is included as is a list of patents of interest. The references in the supplementary list and the patents were reviewed by title or abstract only. The patents were not reviewed fully because of delayed delivery. The references included in the supplementary list were less readily available, or in the reviewers' opinion, dealt with material at least partially covered in the papers which were read in full. Also, a number of the references in this list dealt with equipment or materials, rather than processes, and for this reason were considered of secondary interest at this time.

It is anticipated that the text of this report, as well as the bibliography, will prove to be of value to technical personnel interested in the research, development, or operational phases of high temperature metallurgical processes. The bibliography contains several references to literature of textbook nature which should be useful to persons desiring to acquire an acquaintance with the metallurgical refining field in general.

ABSTRACT

A survey of post-World War II literature related to high temperature metallurgical refining processes and techniques is reported. The processes reviewed are grouped in seven general categories according to the mechanism by which refining or separation is accomplished. The categories selected are: slagging and fluxing reactions, which are important in the tonnage refining of several metals and alloys of commercial importance; gas-solids reactions in which the reaction of a gas with a metal or compound is used to reduce a compound to metal or oxidize a metallic compound; zone refining, a method of producing very pure ingots by segregating the impurities in one end of the ingot; electrochemical refining in a high temperature electrolyte bath; metallothermic reactions in which the desired product metal is displaced from a compound by another metal having a greater affinity for the negative ion of the compound; liquation-segregation and liquid extraction processes in which separations are accomplished by virtue of solubility differences of a solute metal in metallic or other solvents; vaporization, condensation, and vacuum operations in which boiling points and vapor pressures of metals and impurities are utilized to effect a desired separation. A complete bibliography of the papers read, a supplementary reference list, and a list of patents are included.

Selection of refining processes by consideration of melting points and volatilities, thermodynamic data, and alloy phase diagrams is possible when such data are available. A brief discussion of these process selection criteria is included.

A summary in which an attempt has been made to convey the authors' impressions of the current status of the refining processes mentioned is presented.

SUMMARY

The types of processes which have been collected under particular headings in this report are enumerated below with a statement of the authors' impression of the current status and potentialities of the process.

Slagging and fluxing reactions are utilized in the production of pig iron, open hearth steel, fire-refined copper, and other metals of commercial importance. Advantages of the method are adaptability to large scale operation, flexibility of product composition and low cost of operation. Rather precise control of the composition of the product metal is possible in some cases. The degree of removal of any element is a function of its equilibrium distribution between the slag and the melt. A slag or flux mixture must be selected with proper constituents for removal of the undesirable impurities of the melt. This selection is empirical at present. Slag disposal or utilization is a problem not yet solved to the satisfaction of refinery operators.

Gas-solid reactions comprise a varied group of oxidation or reduction reactions as well as more complex exchanges. In general the processes reported are not at present in commercial use, but the sponge iron process, although controversial in certain aspects of technology and economics, is operated successfully in Sweden. At present, however, little except results of laboratory scale work is being published in this area of investigation.

The zone refining technique introduced by workers in transistor research has received a great deal of attention and has produced some excellent results. However, only small ingots of relatively pure metals have received a "finish" refining by this method. For simple cases the mechanism is well defined analytically, and for complex cases, i.e., ternary or multi-component systems, certain predictions can be made from theoretical considerations. Certainly the method holds promise of developing into a specialized metallurgical refining technique, but no estimate can yet be made of its ultimate application.

Electrochemical refining in a high temperature electrolyte bath has been used to produce metals on a commercial scale. Powdered metals of high purity have been produced by this method and the refining of a soluble metallic anode might be an economical method of reworking scrap metals. The author of one of the articles reviewed observes that alloy refining by fusion electrolysis shows definite promise and merits investigation by electrochemists. Theory of electrochemical refining is well defined, but in any new process the practical aspects remain to be worked out, and the practice may diverge from theory because of seemingly minor outside influences.

Metallothermic reactions are widely utilized to produce relatively pure metals from their oxides or other compounds. The preparation of the pure compound is the first essential step. Thereafter, the process consists of replacing the desired metal with another while avoiding contamination of the products. Energy economy and simplicity of operation are two advantages claimed for the process. This process is used to produce refractory and hard-to-produce metals in laboratory scale equipment as well as in commercial operation.

It is advisable that any potential application of the method should be evaluated only after experimental data are available.

Liquation-segregation processes are in common use in non-ferrous metallurgical refining. Formation of intermetallic compounds plays an important part in some of the separations. The method is effective where favorable phase relationships exist. Feasibility of a liquation separation can be determined by study of the phase diagram involved, but should in any case be verified by experiment since impurities or intermetallic compounds may alter the expected results. Amalgam and liquid extraction metallurgy have potential applications in refining, and a desirable feature exists in that extremely high temperatures are not required. The mechanisms employed in amalgam metallurgy are fairly well understood and the method lends itself to small scale experimentation. Amalgam metallurgy was used by the Germans in reclaiming scrap aircraft aluminum, and large scale operations are known to be practicable.

Processes involving vaporization, condensation, and related operations have gained considerable importance in metallurgical refining. These methods have long been employed in refining metals with a lead or tin base and, with the advent of commercial vacuum equipment, have come into use with higher boiling metals and alloys. A considerable amount of accumulated experience is available in the literature and detailed descriptions of equipment and procedure are published. There is a great deal of research activity in the vacuum metallurgy field at present, particularly where high purity is absolutely essential for obtaining physical properties desired in a metal or alloy. Distillation, degassing, melting, and other operations advantageously conducted under vacuum promise to become more common as refractories, retorts, heating elements, and vacuum pumps become less expensive and more economical to operate and maintain.

It should also be stated here that the practice of process and refining metallurgy, although largely empirical, is being revised as new data and correlations appear in the literature. Such work as that reported in the section on "Criteria for Selection of a Separation Process" should have a definite favorable influence on the logical development of future research in the area of refining and process high temperature metallurgy.

REPORT OF A LITERATURE SURVEY
OF
HIGH TEMPERATURE METALLURGICAL REFINING PROCESSES

Introduction

The purpose of this report is to present the results of a survey of recent literature on the separation and refining of metals by means other than aqueous, or other predominantly chemical methods of treatment. In general, the processes considered are conducted at elevated temperatures. Separation of groups of metals from other groups of metals, separation of specific metals from groups of metals, and separation or removal of non-metallic impurities from metals or alloys have long been common metallurgical operations and reports of operations of this nature were sought in the literature of the metals industry.

In the years since World War II, demands for pure metals and alloys of closely controlled composition and properties have given impetus to considerable investigative work in methods of production of these materials. This work has taken several courses, some of them leading to developments in fields not common to traditional metallurgical practice; the new demands for specific metals and alloys have fostered new methods of production, many of them novel in concept or execution. Inert atmospheres, high vacuum, high temperatures and pressures, and electrical methods of heating have been used extensively in many of these operations, and in general the high purity and control have come at the expense of increased capital and operating costs. Many of these processes are established commercially and others probably will be so established in the future, but cost data have not appeared in the literature to any extent, and are not reported here. As would be expected, quantitative data and theoretical developments are far from being equally available for the several processes reported, and the volume of the literature surveyed for any category is roughly proportional to the volume of such literature which has appeared since World War II.

The older metallurgical processes of both ferrous and non-ferrous refining are widely practiced, but not fully developed theoretically. For instance, slagging reactions which are complex oxidation-reduction and solution exchanges are not explained as quantitatively in the literature as would be expected, and there is even considerable disagreement of authors regarding the function of various slag components. The physical chemistry of the reactions of slagging and similar operations is not well defined because of the difficulty of collecting data from actual commercial operations, and this same statement may be made concerning several refining processes which have been widely used almost since

the beginnings of metallurgy. For instance, concerning metallothermic reduction processes, W. J. Kroll, a consulting metallurgist, makes the following statement: "It is still unfortunately the experiment and not the calculation which decides and it is a good habit with the present state of affairs not to put the free energy calculations ahead of the experimental data in any report."

The paucity of fundamental information concerning high temperature refining processes is probably a result of the many experimental difficulties encountered at the temperatures involved. A general lack of technique and apparatus for the necessary investigations has no doubt had a contributing effect. The scale on which these high temperature operations are conducted has a definite influence on the results and there exists a distinct lack of accurate data on mill operations. Since many of these operations cannot be conducted satisfactorily, if at all, on a laboratory scale, this lack of mill data is truly unfortunate.

Slagging and Fluxing Operations

Slagging and fluxing are the most common methods of tonnage refining of metals. The mechanism involved is one of chemical reaction and mass transfer between two liquid phases. Usually, the flux oxidizes the undesired constituents in the molten bath; the oxides are then preferentially dissolved, or chemically combined in the slag.

Richardson (46) concludes that the rate of a slag-metal process is dependent only on the extent to which the two media are out of equilibrium and on the diffusivities of the participating molecules (or ions) in both phases. In support of this idea, comparison is made between the violently agitated ladle desulphurization, completed in minutes during pouring, and the relatively static open-hearth furnace desulphurization which takes several hours.

Carter (6) reviews experimental work on electrical conductivity of slags, slag-metal equilibria of sulfur and oxygen, and various mechanisms of desulphurization processes. Voluminous data indicating slag conductivities as high as those of molten salts support the theory that the basic and acidic oxides form ionizable compounds wherein the metal from the basic oxide assumes the role of cation. Data on oxygen distribution between slag and metal indicate the existence of non-ionizable oxides and compounds. An attempt is made to correlate the conductivity and distribution data by proposing an equilibrium between ionizable and non-ionizable compounds.

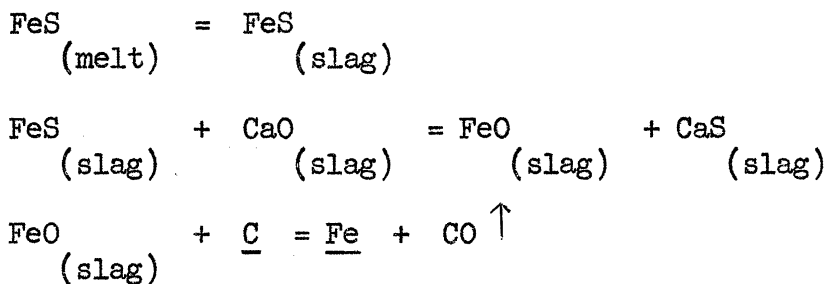
Numerous mechanisms of sulphur removal are examined; several of the more probable equations are discussed in detail.

Herasymenko and Speight (13) assume the ionic theory of slags to minimize the necessary number of slag constituents in steelmaking. Numerous slag-metal equilibria are studied, general effects are summarized, and conclusions drawn where warranted. The following were noted:

- (1) The equilibrium $\underline{O} + S^{--} = O^{--} + \underline{S}$ is independent of other slag constituents.

- (2) The oxygen content of liquid steel and the desulphurization ratio may be calculated from analyses of basic slags.
- (3) Dephosphorization is governed by the reaction $2 \underline{P} + 5 \underline{O} + 3 \underline{O}^{--} = 2 \underline{PO}_4^{--}$
- (4) Calcium fluoride (CaF_2) has a double effect on dephosphorization, since calcium ions (Ca^{--}) increase the stability of phosphate ions (PO_4^{--}) and fluoride ion increases the activity of ferrous ions (Fe^{++}) and decreases the activity of phosphate ions (probably by a chemical complexing reaction).
- (5) The equilibrium $\text{Fe}^{++} + \underline{\text{Mn}} = \underline{\text{Fe}} + \text{Mn}^{++}$ is dependent on the content of oxygen and calcium ions (O^{--} & Ca^{++}), both ions favoring a reduction of manganese ions from the slag to manganese atoms in the bath.
- (6) Oxygen content in basic steel is a function of the content of ferrous oxide (Fe O), total acids (SiO_2 , P_2O_5 , Al_2O_3) and carbon, and is also dependent on temperature.
- (7) The desulphurization ratio (sulphur in slag/sulphur in melt) is a function of concentration of ferrous oxide and total acids.
- (8) Open-hearth furnace slags very closely approach equilibrium with the liquid bath but are far from equilibrium with furnace gases.

Taylor (59) reviews the field of ironmaking in much the same manner that Carter (6) reviews steelmaking, but without using the ionic theory as a criterion. Desulphurization is hypothesized to take place in a three step process:



The factors favoring silica reduction from the slag are increasing temperature and reduction of ferrous oxide content. Manganese reduction is favored by increase in slag basicity, i.e., increase in content of calcium and magnesium oxides. Nitrogen content decreases with slag basicity. Rate of reduction of ferrous oxide is dependent chiefly on temperature and carbon monoxide content.

The field of fluxing is covered by E. R. Thews (60) for copper and copper alloys. Fluxes are divided into seven groups - Oxidizing, alkaline, boron compound, solvent, chloridizing, reducing, and mixtures - and general and specific applications of each group are stated.

Oxidizing fluxes are composed chiefly of the easily reduced metallic oxides. Selection of the metal oxide to be used is usually based on the desired alloy composition of the melt to be refined. The first function of the flux is to oxidize dissolved gases (hydrogen, sulfur dioxide, carbon monoxide*) to an insoluble state, causing their expulsion from the bath. Next are removed the metallic impurities in order of their heats of oxidization. The suggestion is made to use from .5 to 1.0% flux per addition, with fracture examination after reaction and settling, and with a maximum total use of 2.0 to 2.5% flux.

Solvent fluxes, sometimes termed slagging mixtures, consist of boric acid, borax, alkali carbonates, fluorspar, and glass or other silicates, either alone or, more commonly, in mixtures. Their chief purposes are to take up the oxides present or produced in the metal and to protect the melt against atmospheric influences. It is essential to allow sufficient time for impurities to rise to the surface before slagging and pouring. Each of the various possible ingredients of a solvent flux are added for a particular purpose:

Sodium and potassium carbonates have a high affinity for sulphur and arsenic, as well as for silicon dioxide and antimony oxide. They also prevent excess zinc losses by oxidation or vaporization.

Glass mixtures exhibit a very strong solvent action for all metallic oxides.

Borax and boric acid dissolve most metal oxides, plus sulfur and sulfides.

Fluorspar with silica or lime has a very high solvent capacity for metal oxides. Fluorspar with sodium chloride will remove sulfur, sulfides and metallic aluminum and magnesium.

Ferric oxide is an extremely strong solvent for tin and a few other metals.

Caustic soda, fluorspar, alkali carbonates and iron oxide are all used to lower the melting points and viscosities of glass, silicate, and lime slags.

After skimming off the oxidizing and/or solvent flux or slag, a deoxidizing treatment is usually applied. Phosphorus-copper is frequently stirred into the melt and powdered charcoal or coke is spread over the surface. The phosphorus, besides deoxidizing the metal, also decreases the viscosity, very markedly facilitating the rise of metal oxides, gases and non-metallic inclusions to the surface of the bath.

Howatt (17) reviews modern refining methods for several metals. In fire-refining copper, the bulk of the impurities are removed by oxidation and

*More modern theory holds that only monatomic gases are ever soluble in any liquid metals.

absorption in a slag; sulfur, zinc, and cadmium are partly eliminated by volatilization. Tin, arsenic, and antimony are most easily removed by a basic slag, while removal of lead is most easily accomplished by use of an acid cover. Both cases are most effective with a highly oxidized bath (i.e., with .8 to .9% oxygen dissolved). The oxygen is removed after skimming by covering the bath with crushed coke or anthracite. Agitation to increase reaction rate is effected by thrusting green wood poles into the bath.

A two-flux process for melting and refining magnesium utilizes a thin, fluid-protective flux during melting and then a large addition of a thickener or "inspissater." This thick flux is stirred into the melt and removes magnesium oxides and chlorides by agglomeration. The agglomerated impurities are heavier than the metal and consequently settle to the bottom of the furnace where they adhere to the refractory lining.

Bareis, Wiswall and Winsche (2) describe a technique for removing some fission products from a uranium-bismuth liquid fuel system. Certain rare earths were mixed with the fuel which was then heated with the lithium chloride-potassium chloride eutectic. The rare earths equilibrated between the salt and melt and a proportionate amount of lithium reverted to the metal phase. The transfer is postulated as a slagging mechanism and a model is hypothesized. The process is described elsewhere in this report.

Gas-Solids Reactions

Reactions involving gases as one of the reactants are common in metal refining practice and in almost any high temperature work with metals there is some reaction involving gases. This discussion is confined to reactions which are deliberately promoted and are considered the key reaction in the operation in question.

Hopkins (16) and associates report a process for production of high purity iron in 25 lb. ingots. Starting with a selected Swedish ore, the purification was carried out in two main stages:

- (a) Oxidation of a number of impurities and removal of the oxidation products.
- (b) Vacuum treatment for degassing followed by reduction of oxygen to a low level with dried hydrogen.

Melting equipment consisted of two high frequency induction furnaces, one for melting under oxidizing conditions, and one for melting under hydrogen. Temperatures utilized were in the 1550-1600° C. range. Ingots were poured in a stainless steel mold. Five hours were required for a complete refining cycle. The following composition was obtained in the final ingot.

C	.002 - .004%	Ni	.005 - .007%
Si	.002 - .003	Cr	.001
Mn	.004	Cu	.004 - .007
S	.004 - .006	Al	.001 or less
P	.001		

Powell (44), in a discussion of production of rare metals, mentions the high temperature reduction with hydrogen of oxides of germanium, molybdenum, tungsten, and rhenium and states that combination of metals with hydrogen can be a problem. Therefore, vacuum technique was utilized to eliminate minute amounts of gas from the product metal.

Gulbransen and Andrew (12) experimented with reactions of metals and gases at high temperatures (1200° C. and above) and reduced pressures in an attempt to correlate the results with physiochemical theory. They classified the studied reactions into (1) gas producing reactions, (2) gas removing reactions, and (3) gas exchange reactions, and calculated the thermodynamic feasibility for several reactions with zirconium, tungsten, chromium, iron, and magnesium. The effect of oxide films on overall reaction rates was determined for several metals and reactions. They found that some discontinuous oxide films actually accelerated reaction rates. Curves of weight-gain vs. time were plotted for several reactions and equilibrium vapor pressures were calculated. Results were presented for:

- (1) Vacuum oxidation of zirconium, tungsten, molybdenum, and mild steel.
- (2) Formation of carbon monoxide by reaction of carbon in the metal with surface oxide for the alloy Nichrome V.

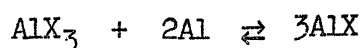
All of these tests and evaluations were executed on a laboratory scale in a vacuum furnace tube.

Gas reactions are often intermediate steps in a complex operation and an example of this case is the method for production of uranium and thorium reported by Chiotti and Rogers (7). The goal was production of a metal powder and this was accomplished by first reacting the massive metal with hydrogen to form the hydride as a powder. The hydride was then decomposed under conditions such that sintering did not occur (300° C. and vacuum for uranium). The operation was conducted on a hundred gram per hour laboratory scale.

Use of a fluidized bed for reduction of nickel oxide was the subject of several experiments by Kivnic and Haxon (21). The experiments were conducted primarily to determine a reaction constant calculated on the basis of weight of oxide available for reaction. The nickel oxide was reduced with nitrogen-diluted hydrogen and the course of the reaction followed by observing the change of hydrogen content of the fluidizing gas entering and leaving the bed. The product at the end of one run was found to be 75% metallic nickel and at that time the bed was still fluidized and no sticking had been observed. The reaction constant was correlated with temperature, gas velocity and time.

Steelmakers have experimented from time to time with the use of oxygen in openhearth furnaces and recently interest in the use of oxygen has received renewed attention. Slottman (52) reports the oxidation of carbon and manganese from an openhearth bath by oxygen injected through a steel pipe which is consumed in the process. Curves on oxygen flow rate vs. bath composition and slag composition are presented. It was found that for removal of relatively small amounts of impurities the oxygen method has several advantages over conventional procedures. High rate of reaction and reduced loss of metal to the slag with reduced time of residence in the furnace are mentioned specifically.

German technicians (1) developed a method of refining scrap aluminum by means of a vapor-liquid reaction. The process depended on the reaction:



Where equilibrium shifts to the right with increasing temperature and X is chlorine, bromine, or other halogens. The operation was carried out by passing AlCl_3 over molten aluminum to form AlCl , then cooling this vapor to deposit metallic aluminum. The normal aluminum chloride was recycled to the process. Operating temperatures of 400° to 700° C. were used. It was not stated on what scale the operation was performed, or what operating experiences were, other than that commercially pure aluminum was produced.

The United States Bureau of Mines has conducted an extensive investigation of methods of producing sponge iron and with other direct iron processes (3). Sponge iron has been defined as the metallic product formed by the reduction of iron ore or other iron oxides at temperatures below the fusion point of iron. The name is derived from the porous nature of the product. When the reduction proceeds at slightly higher temperatures, the particles of metal weld together to yield pellets or balls that lack the porosity and low density characteristics of sponge iron and, therefore, this product is more correctly called "direct iron." The work cited presents a general description of methods that have been proposed or tried for the production of sponge iron or direct iron. The history of sponge iron production has been very discouraging and, in many quarters, it has been written off as not being adaptable to commercial operation. Others believe that the process has a place as a method of supplementary iron production in time of emergency by bringing existing facilities into iron production with a minimum of capital outlay. Brick and cement industry equipment has been suggested for this use.

Sponge and direct iron have been produced by use of several reducing agents, both solids and gases. Reactions in which gases are involved as primary reactants are described in the following paragraphs.

Two methods of reducing iron oxides with gases are credited to Bourcoud and Chenot (3, p. 7). Both carbon monoxide and hydrogen reduce iron oxides. The Bourcoud process, which has never been tried experimentally, depends on high temperature combustion of coal to produce gases of high CO and H_2 content. These gases are reacted countercurrently with preheated iron ore in a helical rotary horizontal kiln where the maximum temperature should be 1300° C. Auxiliary heating would probably be required to maintain the reactor temperature and to maintain conditions conducive to existence of high CO content gases. The process proposed by Chenot utilizes producer gas and a vertical shaft furnace charged with suitably prepared ore and provided with an external heat source. A variation of this process consists of placing electrically heated copper rods across the bottom of the retort to preheat the gases which then flow up through the ore. Complete reduction of the iron oxides was not attained by the Chenot process; forty-five percent metallic iron by weight was reported by one investigator.

Knowledge of physical and chemical properties of iron oxides and available reducing agents are essential to intelligent planning of experiments and for this reason relative reducing potentials of hydrogen, carbon monoxide,

and other gases were investigated by Specht and Zapffe (3, p. 13). They concluded that the best reducing agents are hydrogen and carbon monoxide. Mixtures of gases considered were coal gas, bosh gas, fuel gas, illuminating gas, methane, natural gas, oil gas, producer gas, and water gas. Equilibrium data for the reduction of iron oxides by H_2 and CO are presented graphically. Heat quantities involved in the reduction reactions, measure of reducibility, and the effect of composition of the reducing gas are discussed. CO was found to be an ineffective reducing agent at low temperatures, but hydrogen was efficient in reducing all but precalcined materials as low as $300^\circ C$. CO was found to be the best all-round reducing agent at high temperatures because the iron produced with this agent scaled off leaving fresh iron oxide accessible to the reducing gas.

The Bureau of Mines experimented with a bubble-hearth process (3, p. 61) for production of sponge iron from finely divided ore. The apparatus was similar to a bubble-cap column; the reducing gas was expected to fluidize the bed of small particles of ore on each hearth and reduce the oxides to iron. One device was designed to reduce finely divided ore with hydrogen at $595^\circ C$. Each hearth had an area of 3.7 sq. ft. on which was located 170 bubble-caps on 1 1/2 inch centers. The ore flowed from the upper to the lower hearth while the gas flowed countercurrently. Capacity of each hearth was 600 lbs. of ore. The alloy steel reaction chamber was surrounded by a resistance type electric furnace. Data obtained during four tests of several days duration indicated that laboratory scale work was needed to determine factors effecting fluidization. In the opinion of the experimenters, the laboratory work indicated that the bubble-hearth process was not workable because the difficulties of maintaining the fluidized bed could not be solved by increasing gas velocities alone.

Tests on a shaft furnace 6 inches in diameter by 10 feet-4 inches long (3, p. 62) indicated the feasibility of reducing iron oxide glomerules in an externally heated alloy steel furnace with hot hydrogen or water gas. Using hydrogen as the reducing gas (diluted with 25% nitrogen), iron with an oxygen content less than .50% was produced. Results with water gas were not as good. This unit produced one ton per day of sponge iron on a continuous operating schedule, charging and discharging proceeding continuously. The average entering gas temperature was $800^\circ C$.

Technical feasibility of the reduction of iron oxide pellets by hot reformed natural gas was demonstrated on a pilot plant scale (3, p. 69). Reduction took place in a vertical shaft furnace. The reaction proceeded exothermally at $1025^\circ C$ and the pellets were 95% reduced to metal. The feed pellets were a ferrous oxide slag granulated by pouring it molten into a stream of water.

The work cited (3) also contains literature and patent bibliographies on the sponge iron and related processes.

Blast furnace operation, ore reducing operations on certain non-ferrous metals and steelmaking processes all are dependent on gas reactions, but in general these are rough refining operations in which the gas reaction is but a part of a very complex overall process. For this reason, omission of these topics is not considered detrimental to the purposes of this survey.

Zone Refining

Zone refining, or fractional fusion, is a relatively new process which has been used in the production of ultra-pure metals. W. G. Pfann and co-workers of the Bell Telephone Laboratories first used this method as a means of producing extremely pure metals for transistors. Essentially, the method consists of passing a molten zone through an ingot in the longitudinal direction. If the solubility of the impurity is different in the liquid and solid phases, a concentration difference exists across the phase boundary. Impurities are left behind or carried with the molten zone according to whether they are more soluble in the solid or liquid phase, respectively. Multiple passes are required, the number of passes being determined by the starting composition, required degree of purification, and the distribution coefficient "k", which is the ratio of solute concentration in the solid to the solute concentration in the liquid.

Pfann (41) treats the process mathematically for the case of no solid diffusion and perfect diffusion in the liquid and utilizes the following equation for the concentration of solute at any point in a solid ingot:

$$C = kC_0 (1-g)^{k-1}$$

Where g is the fraction of the original volume which has frozen and C_0 is the original solute concentration in the melt; k is assumed constant. This equation is plotted on a graph of solute concentration vs. fraction solidified with k as a parameter, and the significant relationships between k values and segregation characteristics are outlined. In brief, they are stated: the greater the $(1-g)$ value, the greater the extremes of concentration produced by segregation; for k less than 1 lower k corresponds to faster segregation; for k 's near 0.1 the concentration increases by a factor of about 8 in the first 0.9 of the ingot length. The above relations are for a single zone passage. Pfann extends this development to include the segregation of two solutes and presents calculated segregation curves for antimony and gallium simultaneously segregated in germanium ingots. Where c is the difference of concentration of two solutes, a critical ratio r_c is found for which c will go through a maximum at any desired location.

Pfann (40) discusses the use of the zone melting technique to produce stepped or graded concentrations in an ingot by simple melting and refreezing with one or two solutes. The process is not truly a refining operation, but one of producing controlled variation of composition in a semi-conductor.

Tanenbaum, Goss and Pfann (58) report reduction of impurities in antimony and tin by a factor of ten. The impurities were lead, copper, and iron. Development of a reciprocating induction heating device is also reported. Of several methods of maintaining traveling zones, the authors prefer the reciprocating technique.

Pfann (39) discusses zone melting with applications to zone refining and presents calculated curves for multiple-pass zone refining with solute concentrations and length of ingot solidified as coordinates and k as a parameter. Ultimate distribution of solute after infinite zone passes is discussed and developed mathematically and calculated concentration vs. length solidified

curves with number of passes as a parameter show the nature of this limiting distribution. Zone leveling is the process of homogenizing an ingot by passing molten zones through it in alternate directions. This method is very effective for distributing solute in a metal or alloy which is heterogeneous when charged; uniform concentration of solute is produced in all but the last zone to freeze. An alternate method of zone leveling is to pass successively several zones through a toroidal ingot.

When a molten zone traverses a long solid ingot in a level, open boat, the ingot becomes tapered. Pfann (38) shows that such matter transport by a molten zone arises from the volume change on melting and corresponds in magnitude and direction to the magnitude and sign of the volume change and the mechanism of matter transport is similar to the mechanism of solute transport. The two processes are described by similar equations and it is shown that by inclining the boat at a critical angle, matter transport can be prevented.

Schumacher (49) shows that degree of purification depends on the following factors:

- (1) Initial impurity level.
- (2) Number of passes.
- (3) Difference in solid and liquid solubilities.
- (4) Length of zone.

By proper manipulation of these factors, impurities in germanium have been reduced to one atom of impurity per 10^8 atoms of germanium.

C. H. L. Goodman (10) suggests that the process of zone refining might better be termed "fractional fusion" because of the similarity of the process to conventional fractionating operations as practiced in chemical engineering. He cites the importance of the same variables listed by Schumacher (21), above, and extends previous theory to include binary alloy systems and considers the effect of several types of binary alloy phase diagrams on zone refining. In general, high-melting components are concentrated in the first part to freeze and low-melting components in the last part to freeze. This applies also to stable intermetallic compounds. These compounds can be concentrated by fractional fusion, but not decomposed. Effect of a "peritectic jump" is discussed, and it is shown how this "jump" prevents preparation of mixtures in a certain composition range.

Effects of thermal conductivity of the metal, energy requirements, number of zone passes for a given effect, and methods of heating are discussed briefly. Metals of low thermal conductivity permit precise zone definition and require less power. Zone passages should be slow with a large number of passes for metals refining. Radio frequency heating promotes good molten zone mixing. Zone travel rates of several centimeters per hour are used even with the very high purities required for germanium. The effects of fractional freezing, the process of passing solid zones through a liquid are discussed and presented graphically.

The author of the paper is optimistic about the future developments of this method of refining and homogenizing.

Lord (29) analyzes the zone refining process for long ingots and many zone passages. Formulas are derived which give impurity distribution in the ingot in terms of a finite series.

Pfann (37) reports preparation of high purity germanium with one part impurity to 10^{10} parts germanium by zone refining methods. Zone leveling is also considered by Pfann in this paper.

The zone refining operation described in the literature has been on a small scale, i.e., ingots 1 1/2" in diameter by 12" long, but the mechanism is well understood and results have been impressive in the applications to preparation of high purity metals.

Gross separations are not reported and simultaneous degassification of the molten zone is not mentioned, although both of these seem to be definite possibilities. Pfann (40) mentions additions to the molten zone, but does not go into detail on the subject. Considerable work on the process has been reported and it appears that there is great latitude for further developments and applications other than those advanced to date.

Electrochemical Refining

Refining of metals by electrolytic means is common in the metallurgy of several commercially important metals. Electrolysis of aqueous solutions, fused salt solutions, and mercury amalgams are mentioned in the literature, but this survey is confined to non-aqueous methods and only these are discussed.

P. M. J. Gray (11) describes procedure and apparatus for obtaining 99% pure cerium by electrolysis of fused cerium trichloride. A graphite pot and a sheathed molybdenum cathode were used, the pot acted as the anode and the molten cerium collected at the neutral bottom of the pot. The electrolysis was conducted at 850°-900° C. Calcium and magnesium pick-up limited the cerium purity to 99.7% to 99.8%. Fifteen gram batches were produced. After subsequent experiments with thermal reduction methods, the author concluded that thermal reduction offered the preferred method of producing cerium on the scale considered.

German technicians experimented with electrolytic methods of refining scrap aluminum from aircraft frames and engines (1, 19). A three-layer process in which a bottom layer of impure melt, an intermediate layer of flux, and a top layer of the pure product were electrolyzed, was used at one plant. The flux consisted of chlorides of aluminum, barium, sodium, and calcium, with the specific gravity adjusted to keep it stable in location between the purified aluminum and the scrap melt. Aluminum migrated, under the influence of an electric current, from the impure melt upward through the flux electrolyte to the pure layer on top. Iron contamination of the anode alloy and magnesium oxide contamination of the electrolyte were major difficulties encountered in the operation of the process.

Powell (44), in a review of production methods for rarer metals, lists lithium, rubidium, caesium, and beryllium as metals produced by electrolysis of their chlorides and beryllium, titanium, hafnium, thorium, tantalum,

and uranium as metals produced by electrolysis of their fluorides or double fluorides.

Lithium is obtained by electrolysis of potassium and lithium chlorides. These must be free from sodium chloride if high purity lithium is required. The electrolysis takes place between 355° and 500° C., using stainless steel cathodes and carbon anodes in an electrically heated steel container. Pure lithium is baled from the surface of the bath.

Mixed rare earth metals (Mischmetall) are obtained by electrolysis of fused anhydrous rare earth chlorides. Molybdenum cathodes and graphite anodes are preferred. The process is not economical at present and separation of the product metals is difficult.

Beryllium and tantalum have been produced from fused double fluorides on a commercial scale. The beryllium electrolysis operation was conducted at 1250° C. and volatile, toxic bath salts caused difficulties which led to abandonment of the process. Attempts to produce titanium and zirconium by this process have failed to yield metals of greater than 95% purity.

Senderoff and Brenner (50) experimented with the electrolysis of alkali chlorides to produce molybdenum. Induction heating and inert atmospheres were utilized to maintain the bath at 900° C. in a graphite crucible 2" in diameter and 6" deep. A tungsten cathode and molybdenum anode in a bath mixture of alkali chlorides and a salt of molybdenum were used to produce a product molybdenum powder chemically determined to be over 99% pure.

An intensive investigation of the electrolysis of K_2ZrF_6 was conducted by Steinberg, Sibert, and Wainer (56) to determine optimum conditions for production of zirconium metal by this method. The process studied was an electrolysis of a fused alkali halide-potassium-zirconium fluoride mixture under a purified argon atmosphere at 790° to 1000° C. The process has been adapted to units of 30 and 250 lb. capacity. The cell consisted of a steel shell, with all graphite interior parts, heated by an alternating current carbon resistance element. The product consisted of a metal-salt agglomerate which was crushed and water-washed to recover 99% pure zirconium powder. The most objectionable cell feed contaminants were found to be water, oxides, and iron. Optimum operating temperature was found to be 850° C.

Electrolysis of fused salts shows promise as a method of producing powdered metals of high purity. Sodium, magnesium, and aluminum are produced commercially by fused salt electrolysis at temperatures above the melting temperature of the metal and are therefore removed in the liquid state. Some twenty metals have been deposited as small crystals or dendrites from fused salt baths below the melting point of the metal. Current density at the cathode determines whether the deposited solid metal is smooth or dendritic. In one test cell a 60/40 KCl/NaCl + 25% FeCl₂ mixture was electrolyzed at 700° C. to produce metal as pure as the best commercial grades of high purity iron at the cathode. A soluble iron anode was used to maintain the iron content of the bath. In another case, starting with a relatively impure feed anode and an alkali chloride bath, carbon, sulfur, silicon, and phosphorus were eliminated and the product iron powder was soft, dense, and free of nitrogen and hydrogen. Powder metallurgy fabrication was not attempted with these

powders, but they were sufficiently pure, in fact of higher purity than such powders sold commercially.

In an article on rare-metals metallurgy, Kroll (22) classifies fusion electrolysis operations into (a) metal extraction with soluble or insoluble carbon anode, and (b) metal refining with soluble metal anode. Both of these categories are broken down into subcategories in which the metal product is molten and those in which the metal product is solid.

Calcium can be made by fusion electrolysis of its pure chloride at 850° C. using a graphite anode and an iron cathode at which molten calcium collects. Processes in which the salt and metal are in the liquid state are used for making aluminum, cerium, sodium, lithium, and magnesium from chloride or fluoride baths. With metals lighter than the electrolyte, a contact cathode may be used with a pool of molten metal at the surface of the cell, but this technique is of much less importance industrially than the solid-cathode process.

A table of metals which can be produced by fusion electrolysis with a solid cathode is presented as follows:

<u>Type of Bath</u>	<u>Metals Obtainable</u>
Chloride	Al, Fe, Co, Ni, Cu, Zr, Th, U, Cr, Mn, Ag, Be
Fluoride	Zr, Ta, Cb, U, Be, Th, Ti
Borate	W, Mo
Silicate	Fe
Phosphate	W, Mo

Deposition of metal as a solid may become necessary if electrolytes with melting points higher than that of the metal are not available. In some cases there exists a choice of electrolytes such that metal may be deposited either as liquid or solid. The major problem with the solid deposition method is separation of the salts and metal; separation can be accomplished by aqueous extraction, or vacuum distillation at elevated temperatures.

Alloy refining can be accomplished by electrolytic methods. A solid soluble anode is electrolyzed in a suitable salt bath and refined alloy deposited at the cathode due to differences of decomposition voltages of the bath salts. The author makes specific mention of the refining of ferromanganese in an iron-manganese chloride bath. He is of the opinion that fusion electrolysis alloy refining will be a fertile field for electrochemists in the future.

In another article, a review of current patents on the metallurgy of titanium and zirconium, Kroll (51) criticizes the suggestion that fused salt electrolysis be used as a method of producing titanium from $TiCl_4$. In his opinion, it is a process which is not liable to become practicable for production of commercial purity.

Marden, Lilliendahl and Wroughton (31) discussed the production of thorium and uranium from fused salt baths. In the production of thorium metal

potassium-thorium-fluoride was electrolyzed in a bath of 50% sodium chloride and 50% potassium chloride with a molybdenum strip cathode and the graphite crucible serving as an anode. Thorium is deposited as a powder on the cathode and after removal from the bath is water leached and dried to remove the salt film which protects it from the atmosphere during cooling. Uranium of 99.9+ percent purity was prepared by electrolysis of KUF_5 in a fused mixture of sodium chloride and calcium chloride. A graphite crucible acted as the cell anode and a molybdenum strip as the cathode and the process was similar to that used for thorium production. The operating temperature was $800^\circ C$. Both of these production methods were used to prepare 20 to 30 gram samples of pure metals for research during World War II, and have been superseded as production methods for larger amounts of metal as demand for these metals grew. The methods were simple and practical, and they produced high purity metals from salts of sufficiently high purity. No mention is made of any attempt to scale-up the process.

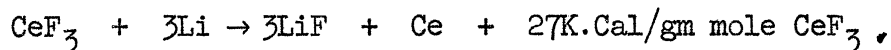
Metallothermic Reactions

The reduction to metals of metal oxides or other compounds by means of a metal having greater affinity for the oxidizing agent than the desired metal is a common metallurgical operation. These operations are known as metallothermic reactions and usually take place at temperatures sufficiently high to yield reaction products in the liquid state and, therefore, easily separable. The charge consists of a finely divided mixture of the reducing metal and the oxide to be reduced; the reaction is usually exothermic, but if the heat evolved is not sufficient to produce molten products at a desired rate, auxiliary heat may be applied. In order to produce pure metals, pure reactants are essential and inert atmospheres or vacuum are often employed to minimize contamination of the product.

Burchell (4) describes aluminothermic processes for preparation of pure chromium, manganese, and special alloys. He states that the reduction to metal of oxides and compounds by means of finely divided aluminum depends on the fact that in combustion of aluminum to oxides the heat of reaction is so great that the alumina produced is in a molten state as a fluid slag and allows the metal to separate readily from it. A relatively low proportion of aluminum is required to liberate a given weight of the product metal, and there is a large saving on fuel usage due to the high heat of combustion.

Aluminum particles varying in size from fine powders to granules are used and it is essential that these particles be well dispersed in the compound to be reduced. Aluminum will reduce oxides of many impurities in the compound and a pure starting compound and pure aluminum are essential to a pure product metal. 99.5% pure manganese has been made from manganese oxide and 99.5% pure chromium also has been made by this method. A ferro-columbium of 65-72% columbium and tantalum (5.5-6.5% Ta) is produced from the mineral columbite in one ton quantities. The author discusses general principles of metallothermic reductions, thermo-chemical considerations, plant equipment, and operating techniques as practiced by the Thermit Metals Group in England.

Reduction of cerium fluoride by lithium was carried out on a fifteen gram laboratory scale by P. M. J. Gray (11). The operation was carried out in a mild steel bomb and proceeded according to the reduction equation:



The cold reactor was put in a Kanthal-wound pot furnace at 1300° C.; in fifteen minutes the outside wall of the bomb reached 1100° C. and the furnace temperature was adjusted to maintain this bomb temperature for thirty minutes, then the bomb was removed from the furnace, cooled, and opened. Cerium had collected at the bottom, flux on top of that, and the excess lithium on top of the flux. Efficiencies up to 85% were achieved. As a result, it was concluded that high purity cerium could be made more satisfactorily on the scale considered by thermal reduction rather than by electrolysis of fused cerium chloride as had been done in a previous experiment. (See section on electrochemical refining.)

The metallothermic reduction of compounds is often but one step in the production of a pure metal from a mineral which occurs in nature, in fact, as a refining operation, it is rather roundabout in that it requires the production of the requisite compound of high enough purity to produce the desired metallic product. Kroll, *et al.* (23) produced malleable zirconium from zircon by the following sequence of operations.

- (1) Production of zirconium carbide from zircon.
- (2) Chlorination of zirconium carbide.
- (3) Purification of raw zirconium chloride.
- (4) Reduction of pure zirconium chloride with magnesium.
- (5) Elimination of residual salts from the metal by vacuum treatment.
- (6) Melting of zirconium ingots.

Step one was accomplished by heating zircon with graphite in a special-design arc furnace, step two by reaction with chlorine in a vertical silica reaction tube. Purification of zirconium chloride was achieved by subliming raw zirconium chloride and condensing it at 100° C. on a core to form a dense product. Reduction of this purified chloride by magnesium took place in the same furnace used to produce the dense chloride. Vacuum distillation for salt removal was accomplished in a retort, and ingot melting in a vacuum furnace. It is seen that considerable equipment and technique is necessary to win pure metals from naturally occurring compounds, even though the key metallothermic reaction is relatively easy to promote.

Stephens and McClain (57) describe the Kroll process for ductile zirconium, which is the same operation referred to in the above paragraph. The authors give the temperature of conversion of ZrO₂ to carbide as 1900° C. and 600° C. as the temperature for distillation of the raw chloride. The pure chloride was resublimed from the cooling coils on which it was condensed; the vaporous zirconium chloride reacted with molten magnesium at 825° C. Purification of the chloride and the magnesium reduction are carried out in a stainless steel retort heated in a pit-type electric furnace. This is the commercial method for production of high purity zirconium in 150 lb. batches.

In the production of the less common elements, reductions of compounds by metals at elevated temperatures are important. Kroll (22), in a review of current (1948) practice and technology, lists manganese, chromium, and vanadium as metals which can be produced by reduction of their oxides by aluminum. Volatility of the metals to be produced is a factor. The temperature of the reaction may exceed the boiling point of the more volatile product metals, and excessive losses may occur. If a reducing agent with a low boiling temperature is used, a similar difficulty is encountered in conducting a reaction. Some of these reactions involving volatile products or reactants can be influenced by controlling the pressure, but in general it is desirable to have the reaction taking place between the melting and boiling points of all the compounds and elements involved.

Reduction of halogen compounds may be used to produce pure metals and the compounds used may be solid, liquid, or gaseous. A large choice of reducing agents exists. Sodium, calcium, and magnesium are high on the chloride affinity series. A table of affinity series based on heats of reaction at room temperature is presented for oxides, chlorides, carbides, and aluminides. However, production of a pure compound is prerequisite to production of pure metals, and a chloride free of oxides or other impurities is usually difficult to produce. Fluoride reduction is also a possibility, but usually melting points of fluorides are higher than of chlorides and, therefore, higher operating temperatures are required. Alkali metal fluorides are the only fluorides that show appreciable solubility in water, and if it is necessary to purify the product by leaching off excess salt, alkali metals with attendant low boiling point problems must be used for the reduction in order to have a soluble fluoride product which can be leached from the desired metal. This fluoride reduction method was used to produce tantalum in Germany, but fluoride chemistry is generally obscure in this field of application.

The following items are taken from a review of patent literature on titanium and zirconium (24). Titanium oxide has been reduced with calcium metal to produce titanium with an oxide content of less than 0.07%. Nitrogen is soluble in calcium and for this reason calcium is not used for the "rough", or first reduction, but only for a refining operation in which the calcium is present in small enough quantities that nitrogen transfer to the product titanium is tolerable. Several patented methods of production of titanium from $TiCl_4$ are reviewed critically and in the author's opinion they are of limited merit. However, they do comprise a cross section of current thinking in the production of titanium by metallothermic reduction. Several of the patents are on processes which were supposedly designed for continuous operation and are of interest from that standpoint.

The relative merits of magnesium and sodium as reductants for $TiCl_4$ are considered. The author concludes that magnesium reduction has decided advantages, particularly the wide temperature range of possible application in the liquid state. The temperature range for liquid operation with alkali metals and their salts is very narrow.

Powell (44) reviews metallothermic methods of producing rarer metals. He states that aluminum has disadvantages which limit its use, although it is probably the most powerful metallic reducing agent. The disadvantages which

are most objectionable are (a) aluminum tends to alloy with most metals, and (b) commercial aluminum usually contains objectionable metallic impurities which appear in the product metal. The latter difficulty is overcome by use of high purity aluminum, but no solution is yet available for the former. The author states also that aluminum is suitable as a reducing agent for volatile metals. Magnesium, strontium, and barium are mentioned as metals which can be produced by reduction of their oxides in vacuo. Powell's perspective of aluminum as a reducing agent is not the same as that expressed above by Burchell.

Calcium can be used to produce vanadium, niobium, thorium, uranium chromium, and some of the refractory metals from their oxides. Some of these reactions, the reduction of vanadium pentoxide for example, must take place in a bomb in order to confine the volatile calcium to the reaction area. A large excess of calcium metal is charged with the reaction mixture. Calcium chloride is also charged in order to dissolve the lime formed in the reaction and to limit the rate of reaction. The reaction is initiated by heating the bomb to 700° C. At this temperature, the reaction takes place almost instantaneously. The product is a solid mass, from which calcium is washed with water. The lime is leached from the reaction mass with dilute hydrochloric acid. The vanadium contained about 0.4% oxygen and the yield was low. The scale of the equipment used was not stated.

The rare earth metals have been the materials studied in some research on the electronic structures of elements (36) (37). For research of this type, it is essential that the metal be of high purity. Spedding, et al. (53, 54) have obtained high purity rare earth metals in the massive state by means of metallothermic reductions of rare earth halides. They established that cerium, lanthanum, neodymium, and praseodymium metals can be produced in a very pure state with high yields by reduction of the rare earth chlorides with calcium. The preparation of samarium and yttrium metals was accomplished, but the yields and quality of the metals were poor. A 2 1/2" by 12 1/2" bomb with a screwed cap and a refractory oxide liner were used in the experiments. A "booster" reaction between iodine and excess calcium was used to elevate the final temperature in order to facilitate the separation of metals and slag. Anhydrous zinc chloride was also used to give an easily agglomerated alloy of zinc and the rare earth metal. In order to initiate these reactions, the bomb was placed in an oven at 650° to 750° C. When the bomb reached 400° C., the reaction took place almost instantaneously. Additions made to the charge in an effort to promote slagging also gave good results. Many 1600 gram reductions were carried out to produce cerium metal. In all 1000 lbs. of 95% to 99% pure cerium metal containing calcium and rare earth metals as the impurities were produced in 1600 gram batches. The production of the other rare earths was carried out on a kilogram scale with the same technique and result as with cerium.

Some purification of metals of the rare earth series is possible by vacuum distillation. Calcium and magnesium distill at about 1000° to 1250° C. at a vacuum of less than 50 microns. Typical of the purification possible by this method is the table of analysis which follows:

<u>Sample</u>	<u>Rare Earth Impurities</u>	<u>Other Impurities, p.p.m.</u>			
		<u>Ca</u>	<u>Mg</u>	<u>Fe</u>	<u>Th</u>
Lanthanum	not detected	150	200	20	not detected
Cerium	not detected	150	250	100	not detected
Praseodymium	.06% Sm, .09% Nd	300	250	700	not detected
Neodymium	500 p.p.m. - 600 p.p.m. Pr; others not detected	300	250	700	not detected

Much of the literature on metallothermic reduction processes was found to be reviews of prevailing metallurgical practice or reports of experimental work. Any data given are pertinent only to the specific reaction under consideration. The publication of fundamental data which would permit process design from these data is lacking. Although some data of this type are available, none were referred to by the authors of the papers reviewed. Some of the experimenters in the field state that free energies of formation may be used to predict the feasibility of a reaction, but that usually these free energies are not available for elevated temperatures. The effects of other variables are not often specifically understood either. Apparently, the caution of the authors in making predictions or generalizing results is well founded.

Liquid Extraction and Liquefaction-Segregation Processes

The differences of solubilities of metals in other molten metals or salts are the basis of several methods used to separate metals from other metals or alloys. The solvent metal or salt is handled in the fluid state, but the solute can be solid or liquid. Segregation and liquefaction operations are common in non-ferrous metallurgy. Fused salt extraction and amalgam metallurgy are less common, but are receiving increasing attention in the current research efforts directed toward fundamental examination of processing methods.

Peretti (36) discusses the factors which control liquefaction and offers this definition: "Liquefaction in metallurgy is defined as the process of separating a fusible substance from one less fusible by means of heat without chemical reaction, i.e., by melting one or more of the constituents." The two methods of commercial practice are pot liquefaction which consists of melting and skimming, and hearth liquefaction which consists of melting and draining fluid from the solid cakes. The phase diagram of a particular alloy is of primary importance in determining whether a liquefaction process will be feasible, but effects of density, surface tension, and melting are also important. The particle sizes and relative void sizes in the solid phase and the viscosity of the liquid phase are discussed relative to their effect on segregation operations. One example is given in which the temperature is raised until one homogeneous phase forms. Then the melt is cooled and the high melting phase precipitated as fine particles. The author has attempted to present an outline of the theory of this method of separation.

Portevin and Dannenmuller (42, 43) are more specific in discussing the effect of the phase diagram on separation by liquation. They state that primary crystals can be removed from a freezing alloy by settling, centrifuging, or skimming. This method of formation and removal of primary crystals is preferred for alloys of near-eutectic composition. Formation of primary crystals is conducted with a falling melt temperature. For alloys far from the eutectic composition, a rising temperature and "sponge" structure favor removal of the liquid phase by drawing off, centrifuging, or by application of gas or liquid pressure. The crystals produced by these methods retain some liquid by capillary action and the particular process utilized must be repeated for further refining.

In some refining operations the impurity is combined with added metals to form compounds which separate as a dross that can be skimmed from the surface of the melt. The preferred additions are alkali metals, alkaline earths, zinc, or aluminum. The excess additions can be removed by oxidation. The precise temperature control required for these operations is possible in an electric furnace. The authors give the following examples of commercial applications of liquation metallurgy.

Example (a) Lead and silver form a eutectic at 2.5 percent by weight silver. Silver exhibits a slight solubility in lead in the solidus. Silver-bearing lead is refined by cooling until crystals of high purity lead begin to form. Two-thirds to seven-eighths of the melt is solidified before the phases are separated. The liquid phase is silver-rich. After repeating the process ten times, lead with 0.002 percent silver may be obtained from a feed of 0.1 to 0.5 percent by weight of silver.

Example (b) Iron-tin ores give an alloy of 70 Sn-30 Fe. The iron-tin alloy system contains a miscibility gap in the solid state and the cast metals separate into two layers, the lower one deficient in iron, the upper layer rich in iron. The iron-rich tin is called "hard tin." The hard tin is heated with silicon, which forms FeSi during freezing. The FeSi rises to the top of the mold, leaving the tin-rich phase at the bottom of the mold. The segregated FeSi contains very little tin. After removal of the hard tin from the initial casting, the tin-rich bottom layer is purified by slow crystallization of FeSn₂. The FeSn₂ removes the crystallized remainder of the iron. The FeSn₂-Sn eutectic is very nearly 100 percent tin, and a tin of only 0.05 percent iron is obtained as the final refined product.

Example (c) Addition of a metal to form a separable compound is practiced in the removal of bismuth from lead. Calcium is added to form Bi₂Ca₃ (m.p. 928° C.), which separates as a scum which is removed before oxidizing or chlorinating the lead to remove excess calcium.

Reclaimed airplane scrap was a major source of aluminum in Germany during and after the recent war. Dissolution and liquation processes played an important part in reclaiming the scrap metal (1,19). In one plant, impure aluminum was mixed with 25-30 percent magnesium and cooled to segregate intermetallic compounds which were filtered out before the magnesium was recovered by vacuum distillation. All impurities except nickel and tin were removed to commercial alloy levels. Another process employed mercury as the

dissolving metal. The scrap aluminum was granulated and dissolved in mercury at 650° C. and 22 atmospheres pressure. All metals except iron, silicon, titanium, and vanadium dissolved in the mercury. The liquid was filtered twice, then transferred to a cooling chamber where mercury and aluminum separated. The aluminum was washed several times with mercury and the excess mercury removed by vacuum distillation; the mercury was water-washed and recycled to the process.

Zinc and lead were also used to refine aluminum. Impure aluminum was mixed with several times its weight of zinc, then treated by liquation and filtering to remove Fe and Si which were thrown out as FeAl₃ and elementary silicon. Iron was reduced to 0.02 percent. Lead was used in another process as follows. Aluminum is 1 percent soluble in lead at 1000° C. and of very slight solubility at 600° C. Impure aluminum was dissolved in lead at 1000° C., undissolved iron and silicon removed from the melt surface, and the aluminum recovered by cooling the melt to 600° C. Excellent purification of aluminum was achieved, but fuel and cooling costs for heating the great masses of lead were prohibitive. Lead was removed from the aluminum by addition of sodium which brought the lead to the surface as a dross to be skimmed off.

Where filtering was used in separations discussed above, beds of crushed quartz with graded particle sizes gave a filtering rate of several hundred kilograms per hour for a square decimeter of bed. Vacuum filtration was employed extensively.

St. Clair (55) reviews the history of refining metals and alloys by filtration and reports the results of experiments on the filtering of lead, zinc, tin, and aluminum alloys. Fine wire screen filters were used successfully in filtering lead. Stone filters worked for higher melting metals but were found to plug with some metals and impurities. For this reason, granular filter beds were substituted and found to be satisfactory.

In general, the process consists of melting the alloy to be processed and then cooling to just above the melting point before filtering out the fine crystals which form the solidus phase. This phase may be a nearly pure metal, an alloy, or an intermetallic compound.

The iron content of zinc was reduced to 0.06 percent by filtration through chamotte filter plates. These filter plates were found to be essential for removing the fine crystals which passed through the granular beds. The yield of metal in the filtrate depends on the amount of iron to be eliminated in the residue, also on lead, copper and cadmium being simultaneously removed. One sample left 45 grams of residue from 16,000 grams of feed melt, the remainder appearing as filtrate.

St. Clair also describes two aluminum purification processes in which filtering and formation of filterable intermetallic compounds were employed by German technicians. Phase diagrams are shown for the alloys in question and interpretation of results as related to phase diagrams is included.

Centrifugal separation of liquid and solid phases from binary alloys is discussed by Schellinger and Spendlove in a Bureau of Mines Report (470),

The centrifugal apparatus used was a 3 inch spinner pot which was revolved in a gas fired furnace at speeds up to 3000 r.p.m. The efficiency of centrifugal separation of liquid from solid phases was investigated by comparing experimental results with the theoretical separations predicted from equilibrium phase diagrams. In general, the efficiencies recorded were over 90 percent. Separation of intermetallic compounds from alloy melts was also accomplished with efficiencies of over 90 percent. This intermetallic compound separation may have application in cases where a metal is added to a melt to form a compound of different density with one of the metallic impurities in the melt. Metal-slag separations should also be readily promoted by centrifugation.

The centrifuge was constructed of mild steel and not intended to be operated at temperatures over 500° C. After extended operation at 500° C., corrosion or other deterioration was of a minor degree only. One operation was conducted at 900° C. with no detrimental effects. Lead-bismuth, lead-magnesium, lead-antimony, and lead-tin alloys were separated by centrifugation at various temperatures. Data and interpretation of results with respect to phase diagrams are included in the author's discussion.

Hohn (14, 15) outlines the principles of the applications of mercury amalgams in chemical metallurgy. Mercury amalgams are divided into three groups which are defined by naming a metal typical of the group. The groups, typified by three degrees of affinity for mercury, are the iron, zinc, and sodium types. Sodium types unite exothermally with mercury; zinc types have good affinity without excessive heating and form mixed crystals; iron types amalgamate only in the nascent state. In general, metals of the zinc type are most soluble, and metals of good solubility are next to mercury horizontally and vertically on the periodic table. An expression for the potential of amalgams and a chart of potentials is given by the author. Solubility increases markedly with increasing temperature and solubility is not always apparent superficially, for metallic suspensions often combine with soluble components and precipitate the product. Amalgams are usually handled in the fluid state at room temperature, but temperature and pressure have been manipulated to give a desired separation.

Separation of mercury from the dissolved metals is usually by distillation which is "dry" for the iron types and "wet" for the sodium and zinc types. In the wet distillation, an ingot is left while in dry distillation the residue is a powder.

The author discusses several applications of amalgam metallurgy in refining and ore processing operations and proposes the use of lead and zinc for selective dissolution of individual metallic components from metallic systems. He claims that a great advantage of these techniques is the reduction of energy requirements.

Use of a liquid fuel has several advantages in nuclear reactor design and operation. A fuel alloy of molten bismuth and uranium has been used, on an experimental basis, as a nuclear fuel. Continuous reprocessing of the fuel material is one of the most attractive possibilities of this alloy.

Baries, Wiswall and Winsche (2) conducted experiments on the separation of uranium from fission products with potassium chloride-lithium chloride salt mixtures at 450° C. A separation factor defined as

$$\left(\frac{\text{rare earth in the salt/rare earth in the metal}}{\text{uranium in the salt/uranium in the metal}} \right)$$

was found to have a value in the order of 10^4 . A fourth power relationship was shown to be valid for the ratio of rare earths in the salt and in the metal. Lead, tin, and polonium favored the metal phase, plutonium was found in both phases, and barium and neodymium went mostly into the salt. Addition of sodium made the metal phase retain more uranium and rare earths. The bismuth could be purified of base metal impurities by selective chlorination. The authors hypothesized that the phase exchange of rare earths took place by a slagging reaction, rather than by solution, and theory and experiments support this view.

The authors state that the lithium chloride-potassium chloride salt system should be effective in separating uranium from elements in columns 1A, 2A and 3 of the periodic table. This system is limited by the fact that alkali metal is transferred to the fuel alloy with resultant poisoning and also by the sensitivity of the salt phase to small amounts of oxidizing or reducing impurities. Buffers or BiCl_3 additions might solve these problems. The selectivity of the chlorination is such that two chemically similar elements may be cleanly separated if the free energies of formation of their halide differ by only a few kilocalories. In most cases, a good separation should be obtainable in a single stage and if countercurrent contacting equipment can be devised, almost any pair of elements should be separable in an appropriate salt-metal system.

It is seen that the extraction and purification methods described are in most cases the result of experimental and not theoretical work. Perhaps this can be explained by the fact that, with the exception of mercury amalgams, the systems are not well understood or are not amenable to analytical treatment. Whatever the explanation, the fact remains that metallurgical research in these fields has been chiefly experimental.

Vaporization, Condensation and Vacuum Operations

Separation of metals or impurities from metals is sometimes effected by distillation or sublimation. The vapor or the residue may be the desired product. If the vapor phase contains the product, a condensation step is used to recover the desired components.

Since the melting points of metals are generally relatively high at atmospheric pressure, many commercial and laboratory vaporization and condensation operations are conducted at reduced pressure. Kroll (25, 26, 27) reviews the field of vacuum metallurgy in detail, including theoretical and practical considerations for laboratory and plant scale operations. He discusses actual and potential uses of vacuum metallurgy in terms of the properties of the metals being processed.

Vacuum evaporation of metals is shown to be a purely surface phenomenon, as contrasted to more common evaporations in which boiling can occur. Metals, by nature of their densities and thermal conductivities, do not ordinarily boil, therefore a large surface area and adequate agitation must be provided if the metal is to be vaporized at an appreciable rate. Instant removal of the vapor is essential due to the large volume of vapor represented by a given mass of metal at the very low pressures used.

Location of the triplepoint is important since it determines whether the metal can be condensed over the melt surface or whether refluxing will take place. Condensation at a surface over which the vapor is traveling downward is preferred, and it has been found in practice that a metal-vapor pressure of 1.8 mm. Hg is a minimum for economical operation. Temperatures at 1.8 mm. Hg are recorded for a number of metals of industrial application.

Where a choice of condensing in liquid or solid form is presented, the following factors should be considered:

- (1) Solid condensation results in low heat transfer coefficients in the condenser and provision must be made for removal of the crystals formed. Fractionation of vapors is not easy, but in certain cases good separations have been achieved.
- (2) Liquid condensation offers improved heat transfer and fractionation possibilities which have not been developed to date.

Sublimation has advantages in some cases, but low heat transfer rates and surface films of nonvolatile impurities may be a problem. With metals of very high melting point, no choice of evaporation methods may exist and sublimation may be the only practical way to produce a vapor.

In addition to making possible the reduction of process temperatures, vacuum techniques may be used to influence reactions which have gaseous reactants or products. At a given temperature, for example, reactions between carbon and oxides can be carried farther in vacuum than at atmospheric pressure because the gases produced are removed from the reaction area, shifting the equilibrium point of the reaction. These reactions take place at the surface because the high density of metals causes a rapid increase of pressure with depth below the surface of the melt. Adequate stirring is essential to maintain a supply of reactants at the surface. Removal of gaseous impurities proceeds simultaneously in the melting step in vacuum operations.

Several examples of vacuum distillation processes are given, among them are a lead distillation purification, removal of magnesium and magnesium chloride from zirconium and titanium, and separation of copper-base, lead-base and tin-base alloys. Fractional distillation and condensation of inorganic compounds also has possibilities for the reclaiming of drosses and separation of metals from solutions used in fusion electrolysis operations. Inter-metallic compounds and the influence of their heat stability on results, as

well as how they may be used to influence results, are discussed. In these three articles, the author mentions a great number of applications of vacuum techniques in metallurgy, some of them in commercial use, but most of them as yet undeveloped.

In the Kroll process for production of malleable zirconium (23, 57), a sponge metal is produced. The pores of the sponge zirconium are filled with excess magnesium and magnesium chloride product from the metallothermic reduction of zirconium chloride. The magnesium and magnesium chloride are removed by vacuum distillation in a stainless steel externally electrically heated retort. This method is in commercial use and at the present time is the process used to produce a major share of the zirconium used in the United States.

Vapor deposition is a process first experimented with in connection with manufacture of tungsten electric lightbulb filaments. Essentially, it consists of passing a vapor of a metallic compound over a heated surface, which causes decomposition of the compound and plating of metal on the hot surface. Campbell and Powell (5) state that an atmosphere of a volatile metal chloride mixed with hydrogen has been used experimentally, and that, since the temperature need only be high enough to effect a reasonable reaction rate, deposition may be carried out far below the melting point of the metal, i.e., tantalum which melts at 3000° C. can be deposited at 500° to 600° C. The deposited coatings are said to have the same properties as fused metals of comparable purity. By reactions similar to those used for deposition of metal coatings, refractory coatings such as carbides, borides, nitrides, silicides, and oxides may be deposited. A table of some seventy possible deposition reactions is presented, and sketches of laboratory scale induction heating and plating equipment are presented.

Despite the wide variety of chemical reactions involved, the coating procedure is substantially the same in all cases. The plating atmosphere is forced past the heated underbody and by-products are pumped from the system or condensed in the exhaust. An inert carrier gas or a vacuum are often used. Industrial applications of the method are predicted in several fields.

Picard and Joy (18) describe an apparatus for vaporizing metals in a vacuum by high frequency heating. A fused quartz crucible was used, but no crucible material was found which was suitable for use in more than one melt cycle. Degassing was accomplished in the melt cycle and care was taken that the gas pressure in the vessel did not exceed 10^{-4} mm. of Hg. lest the gases become ionized and dissipate the power of the high frequency field. The experiments were conducted on a laboratory scale using a bell jar as a vacuum vessel.

Spedding, et al. (53) developed a method of producing rare earth metals by metallothermic reductions. The rare earth metal ingots are purified of calcium of 1 to 5 percent concentration and magnesium of 0.1 to 1 percent concentration by vacuum distillation. The residual rare earth had less than 200 p.p.m. of either of these metals in it. The distillation was carried out on a laboratory scale, the ingots were in the 100-200 gram weight range.

Cook and Wartman (8) report on the operation of a vacuum distillation apparatus for removal of magnesium and magnesium chloride from titanium metal sponge. The crude mixture was heated to about 1700° F. and the magnesium metal and chloride were volatilized away from the titanium, leaving it practically magnesium-free sponge. Several tons of metal have been treated in this way with results superior to those obtained by leaching or grinding. Retorts with a 200 lb. capacity were used to treat 300,000 lbs. of titanium over a period of several months.

The retorts consisted of charge containers, heating elements, and condensers inside a single shell. Downward condensation was employed and distillate was removed from the charge through holes in the bottom of the charge container. Mild steel was used in construction of the retort, which had an overall diameter of 18 inches. The outside diameter of the furnace shell was about 3 1/2 feet. Equipment, operation, and results are presented in detail.

Vacuum methods of separation of lead, cadmium, and germanium sulfides from zinc sulfide concentrates were investigated by Kenworthy and Absalom (20). The goal of this investigation was a higher percentage of extraction of lead, cadmium, and germanium than is common in practice. Volatilization of the desired sulfides in inert atmospheres and in vacuum was conducted in an electrically heated chrome steel tube furnace. Experiments were conducted at 700°, 800°, and 900° C. and percent removal vs. hours of treatment plotted for several conditions. A description of the process and equipment is presented in some detail.

Vacuum operation is sometimes resorted to as a method of producing metals of high purity when refining, alloying, or casting. Nesbit (33) experimented with vacuum induction furnace operations operating at less than 50 microns pressure. The vacuum furnace used was provided with a mechanism for making additions to the melt. Conventional induction heating coils were used. At 440 volts, 960 cycle current was found to give good melt stirring while 10,000 cycle was found to be advantageous for heating small particles. A 25 kw. power source melted 6 lbs. of metal in 5 to 10 minutes and temperatures in excess of 3600° F. were reached. A cycle consisting of melting for degassification, solidification, additions, remelting, and cooling required less than one hour. Several hundred alloys have been melted in the apparatus, which is described in detail.

Kroll and Schlechten (28) review the literature on the reactions of carbon and metal oxides in a vacuum and report the results of an experimental study of the reduction of several metal oxides by carbon in a vacuum. None of the refractory oxides studied was stable in contact with carbon in a vacuum at temperatures above 1380° C. and oxides of multivalent metals reacted at 700° C. or less. As a method of producing pure metals from oxides, best results were obtained with chromium, vanadium, columbium, and tantalum. Purities in the order of 93-97 percent were attained. A table of temperatures at which carbon and metal oxides first react is presented and the authors conclude that the method would be practical only for production of more expensive and rare metals.

Moore (32) summarizes the advantages of vacuum melting as follows:

1. The metal is protected against atmospheric contamination.
2. Gas-metal compounds can be dissociated and eliminated.
3. Dissolved gases are minimized.
4. Reactions with gaseous products are accelerated

Several investigators describe special vacuum or inert atmosphere furnaces and retorts, but since these pieces of equipment are in quite common use, no extensive search was made for information concerning them. However, in the following paragraphs mention is made of the application of several types of commercial electrical vacuum furnaces and other melting equipment.

Sites (51) describes furnaces and retorts which are commercial units producing hundreds of pounds per batch in vacuum melting operations. Advantages claimed for vacuum melting are gas elimination from the melt and elimination of certain trace impurities. The author describes the different types of vacuum furnaces available and the temperature range in which they are used. The commercial vacuum furnaces are divided into groups as follows:

- (1) Resistance furnaces: The temperature limit of externally heated furnaces is about 1850° F. with resistance elements external to the retort. Temperatures of 2750° F., or higher, are practical with molybdenum or tungsten resistance heaters located inside the retort.
- (2) Induction furnaces: These furnaces are chiefly used for temperatures of 2750° F., or higher, and for degassing operations.
- (3) Vacuum arc furnaces: These furnaces are used for very high melting or reactive metals. A water-cooled copper container is often employed. With a consumable electrode, fusion rates can be accurately controlled.

The author's company is engaged in the manufacture of vacuum furnaces and he presents sketches of several types.

A laboratory scale arc furnace for melting refractory metals is described by Pugh, Hadley and Hennig (45). Melting takes place in an argon atmosphere at about 780 mm. Hg., and the arc is operated at currents up to 1200 amperes at 20 volts. A tungsten electrode is used, the electrode cooling water being circulated through the brass electrode holder. Vibratory feeders are enclosed inside the vacuum shell for making additions to the melt. Semi-continuous casting of an ingot 2 inches in diameter is possible by withdrawing the solidified ingot slowly from the bottom of the melting crucible.

Bar stock up to one inch in diameter has been melted at rates up to 100 grams per minute by drip melting (30). In this process, bar stock is fed into a water-cooled induction coil with no contact with the surroundings. The entire end of the bar is molten and drops fall off intermittently and are collected in a mold. The operation is carried out under vacuum with a 150,000

cycle per second current. Zirconium, titanium, beryllium, and iron were melted by this method. Melting rates of 2 to 3 lbs. per minute were attained using a 3000 cycle generator and a 2 inch diameter rod. An 18-8 stainless steel bar was used in the tests at the 3 lbs. per minute melting rate.

A similar technique developed consisted of suspending a "pancake" coil over a block of metal and melting a puddle to a depth of one inch. Sound ingots of titanium metal were poured from such a melt.

Okress, et al. (34, 35) experimented with a technique of induction levitation with simultaneous induction melting of metals and alloys. Design of a pair of coaxial coils which perform the desired operation is developed for the case of the suspended solid sphere and verified experimentally for both the solid sphere and the molten metal which assumed the shape of a top. Aluminum, tin, titanium, and molybdenum were melted in the interaction space between the two coils and all remained stably levitated. In the levitated state, the molten mass was vigorously agitated and tended to rotate about its axis of symmetry, but this rotation was slow and could be prevented by introducing axial assymetry.

Solid levitation operations were conducted in air and in vacuum without difficulty, but when melting commenced in a vacuum, it was found that dripping of the molten metal could not be stopped. The feasibility of levitating molten metal in a vacuum or a protective atmosphere was not established.

If electromagnetic levitation can be expanded to a larger scale, the author claims the following potential advantages:

- (1) The specimen touches no crucible or container during the heating, melting, and draining stages.
- (2) The heated or molten specimen can be protected by a suitable atmosphere or a vacuum.
- (3) Volatile impurities can be distilled or pumped away.
- (4) The molten metal can be drained gradually or dropped as a whole, and it may even be feasible to solidify the still levitated melt and then drop it solid.
- (5) The melt is thoroughly mixed electromagnetically.
- (6) The specimen can consist of metal powders or alloy constituents sintered together, or bound by a suitable binder.
- (7) Alloy additions can be made while the melt is in levitation.

The authors have as yet been unable to levitate molten metals in vacuum for an extended period. In one experiment ten grams of molten aluminum were suspended for one minute. With other metals, and with larger masses of aluminum, the molten metal dripped from the solid as rapidly as it formed. If molten metals can be levitated in a vacuum, such techniques will offer real possibilities worthy of investigation.

Criteria for Selection of A Separation Process

Until recent years, the processes used for purifying metals have been procedures for controlling previously observed phenomena. Little success attended efforts to explain the basic mechanisms or to correlate the amassed data. Recently, however, there have been several notable papers devoted to establishing basic process selection criteria. Three indexes considered are melting points and relative volatilities, free energies and activities, and relative solubilities in liquid and solid solvents.

Schuhman (48) examined the various phases occurring in pyrometallurgical systems as means of separating metals. He stated, "The broad objective in conducting a unit process is to accomplish certain separations and this is achieved by controlling the distribution of the metal and other elements between the two or more phases formed as products of the unit process."

Some thirty common metals are classified according to melting points and volatilities. Melting points and volatilities are then demonstrated to be controlling factors in selection of certain extraction processes. Metals with low melting points and low vapor pressures, such as lead, tin, antimony, gold, copper, and silver, are commonly smelted and refined by processes yielding liquid metal as a primary phase. High-melting metals, such as molybdenum and tungsten, are generally refined by processes which yield a solid metal. Metals with low boiling points, including zinc, mercury, cadmium, and arsenic, are typically purified by procedures utilizing the gaseous phase at some stage.

Darken and Gurry (9) present thermodynamic free energy data for numerous common metals. Plots of free energy vs. temperature are presented for oxides, sulfides, and chlorides, and activity-temperature charts are given for carbides and nitrides. Since these charts indicate the relative stabilities of the compounds and the relative reactivities of the various metals with certain non-metals, they may be used to predict the feasibility of proposed processing techniques. For example, it can be determined from these charts that titanium dioxide may be reduced to the metal by calcium, magnesium, lithium, or aluminum. Inspection of the charts also indicates that the reduction of titanium dioxide by carbon would not be practical unless the operating temperature were in excess of 1700° C.

Phase diagrams indicate the relative solubility of metals in the liquid and solid phases of other metals for which the diagram is constructed. Precise phase diagrams are available for most common binary alloys and reliable estimates of unavailable phase diagrams can be made using a method derived by Darken and Gurry (9, p. 324). Peretti (36) shows that these diagrams can be used to predict liquation separations, segregation separations and, particularly, what results may be expected in the ideal case of such separations. Zone refining, a special case of segregation refining, can also be considered from the aspect of phase solubilities as indicated by the binary phase diagrams and prediction of separations can be made on the basis of the information provided by an accurate phase diagram.

BIBLIOGRAPHY

1. Anonymous, German technicians, from F. I. A. T. Report, Metals Industry, 71, pp. 447-9, 467-9, 1947.
2. Baries, D. W., Wiswall, R. H., Winsche, W. E., "Fused Salts for Removing Fission Products from Uranium-Bismuth Fuels", Nucleonics, 12, No. 7, pp. 16-19, July, 1954.
3. Barrett, E. P., "Sponge Iron and Direct-Iron Processes", U. S. Bureau of Mines, Bulletin 519, 143 pp., 1954.
4. Burchell, T., "The Aluminothermic Process and the Preparation of Commercially Pure Chromium, Manganese and Special Alloys Such as Ferro-Columbium", Institution of Mining and Metallurgy, Preprint from Symposium, "The Refining of Non-Ferrous Metals", July, 1949.
5. Campbell, I. E., and Powell, C. F., "Vapor Deposition", Iron Age, 169, No. 15, p. 113, 1952.
6. Carter, P. T., "Steelmaking Reactions. Sulphur, Phosphorous, Carbon", Iron and Steel, 26, pp. 297-302, June, 1953.
7. Chiotti, P., and Rogers, B. A., "Production of Uranium and Thorium in Powder Form", Metal Progress, 60, pp. 60-5, 1951.
8. Cook, M. A., and Wartman, F. S., "Removal of Magnesium and Magnesium Chloride from Titanium Sponge by Vacuum Distillation", Bureau of Mines, Report of Investigations 4837, February, 1952.
9. Darken and Gurry, Physical Chemistry of Metals, McGraw-Hill, 1953.
10. Goodman, C. H. L., "Fractional Fusion", Research, 7, No. 5, pp. 168-177, 1954.
11. Gray, P. M. J., "Production of Pure Cerium Metal by Electrolytic and Thermal Reduction Process", Transactions Institute of Mining and Metallurgy, 61, Part 4, 1952.
12. Gulbranson, E. A., and Andrew, K. F., "Reactions of Metals in High Vacuo", Journal of Physical and Colloid Chemistry, 53, pp. 691-711, 1949.
13. Herasymenko, P., and Speight, G. E., "Ionic Theory of Slag-Metal Equilibrium", Journal of Iron and Steel Institute, 166, p. 289, December, 1950, p. 169, November, 1950.
14. Hohn, H., "Applications of Amalgam Metallurgy", Research, 3, pp. 407-417, 1950.
15. Hohn, H., "Mercury in Chemical Metallurgy", Research, 3, pp. 16-23, January, 1950.

16. Hopkins, B. E., Jenkins, G. C. H., and Stone, H. E. N., "Production of High Purity Iron and Iron Alloys on a 25 Pound Scale", Journal of Iron and Steel Institute, 168, pp. 377-82, 1951.
17. Howat, D. D., "Modern Methods of Refining Non-Ferrous Metals", Metal Treatment, 16, pp. 157-63, 1949.
18. Joy, J. E., and Picard, R., "Metal Evaporator Uses High Frequency", Electronics, 24, pp. 126-8, 1951.
19. Kemp, J. T., "German Practice in Refining Secondary Aluminum", Metals Technology, 14, (3), A. I. M. M. E. Technical Publication No. 2143, pp. 14, 1947.
20. Kenworthy, H., and Absalom, J. S., "Separation of Lead, Cadmium, and Germanium Sulfides from Zinc Sulfide Concentrates", Bureau of Mines, Report of Investigations 4876, May, 1952.
21. Kivnik, A., and Haxon, A. N., "The Reduction of NiO₂ in Fluidized Bed", Chemical Engineering Progress, p. 394, August, 1952.
22. Kroll, W. J., "Rare Metal Metallurgy: Special Production Methods for the Less Common Elements", Metal Industries, 73, No. 14, p. 266, No. 15, pp. 283-6, No. 16, pp. 307-8, 310, No. 17, p. 323, 325, 1948.
23. Kroll, Schlecten, Carmody, Yerkes, Holmes, and Gilbert, "Metallurgy of Malleable Zirconium", Transactions Electrochemical Society, 92, p. 99, 1947.
24. Kroll, W. J., "The Metallurgy of Titanium and Zirconium", Metal Industry, 84, p. 325, April 23, 1954, p. 401, May 7, 1954.
25. Kroll, W. J., "Vacuum Techniques in Metallurgy", Times Review of Industry, 7, (new section) pp. 26-28, 31, August, 1953.
26. Kroll, W. J., "Melting and Evaporating Metals in a Vacuum", Transactions Electrochemical Society, No. 87, pp. 571-87, 1945.
27. Kroll, W. J., "Vacuum Metallurgy, Its Characteristics and Scope", Vacuum, pp. 163-83, July, 1951.
28. Kroll, W. J., and Schlecten, A. W., "Reactions of Carbon and Metal Oxides in Vacuum", Journal of the Electrochemical Society, 93, pp. 247-58, 1948.
29. Lord, N. W., "Analysis of Molten Zone Refining", Journal of Metals, 5, p. 1531,
30. Magel, T. T., Kulin, P. A., and Kaufman, A. R., "Approach to Melting Reactive Metals Eliminates the Use of Refractory Containers", Journal of Metals, 4, pp. 1286-88, December, 1952.
31. Marden, J. W., Lilliendahl, W. E., Wroughton, D. M., "Recent Developments in Rare Metals", Steel, pp. 93-4, 124, 126, 130, 133, 1947.

32. Moore, J. H., "Some Aspects of Vacuum Melted Metal", Metal Progress, 64, No. 4, pp. 103-5, October, 1953.
33. Nesbit, J. D., "Producing High Purity Metals with Vacuum", Iron Age, 159, No. 25, pp. 56-9, 1947.
34. Okress, E. C., Comenentz, G., "Electromagnetic Levitation of Solid and Molten Metals", Journal of Applied Physics, 23, pp. 545-52, May, 1952.
35. Okress, E. C., and Wroughton, D. N., "Metals Melted Without Crucibles", Iron Age, 170, No. 5, p. 83, 1952.
36. Peretti, I. A., "Factors Which Control Liquidation in Metallurgy", Engineering and Mining Journal, 148, No. 12, pp. 76-8, 1947.
37. Pfann, W. G., and Olsen, K. M., "Purification and Prevention of Segregation in Single Crystals of Germanium", Physics Review, 89, pp. 322-23, 1953.
38. Pfann, W. G., "Change in Ingot Shape During Zone Melting", American Institute of Mining and Metallurgical Engineers Transactions, 197, pp. 1441-2, November, 1953.
39. Pfann, W. G., "Principles of Zone Melting", Journal of Metals, and Transactions, A. I. M. M. E., pp. 747-53, 1952.
40. Pfann, W. G., "Redistribution of Solutes by Formation and Solidification of a Molten Zone", Journal of Metals, 6, A. I. M. M. E., Transactions, 200, pp. 294-7, 1954.
41. Pfann, W. G., "Segregation of Two Solutes, With Particular Reference to Semi-Conductors", Journal of Metals, 4, No. 8, pp. 861-5, August, 1952.
42. Portevin, A. M., and Dannenmuller, M., "Segregation and Liquation of Alloys and Their Application to Non-Ferrous Metallurgy", Journal of the Institute of Metals, 75, Paper No. 1191, pp. 949-72, 1949.
43. Portevin, A. M., and Dannenmuller, M., "Segregation and Liquation in Alloys", Engineering, 168, pp. 683-85, December, 1949.
44. Powell, A. R., "Problems in Production of Some of the Rarer Metals", Institution of Mining and Metallurgy, Preprint No. 4 from Symposium, "The Refining of Non-Ferrous Metals", July, 1949, 15 pp.
45. Pugh, J. W., Hadley, R. L., and Henning, R. W., "An Arc Furnace for Melting Refractory Metals", Metal Progress, 63, pp. 70-1, March, 1953.
46. Richardson, "The Chemistry of Process Metallurgy", 344 pp., Non-Ferrous Refining Practices, Gurney and Jackson, London, England, 1949.
47. Schellinger, A. K., and Spendlove, M. J., "Centrifugal Separation of Liquid and Solid Phases from Some Binary Alloys", U. S. Bureau of Mines Report, Investigation No. 5007, p. 19, 1953.

48. Schuhman Jr., R., Engineering Principles, Metallurgical Engineering, Vol. I, Addison-Wesley Press, Inc., Cambridge 42, Massachusetts.
49. Schumacher, E. E., "Ultra Pure Metals Produced by Zone-Melting Technique", Journal of Metals, 5, pp. 1428-9, 1953.
50. Senderoff, S., and Brenner, A., "The Electrolytic Preparation of Molybdenum from Fused Salts", Journal of Electrochemical Society, 101, pp. 16-38, January, 1954.
51. Sites, G. J., "Vacuum Furnaces for Melting or Processing of Metals", Metal Progress, p. 161, May, 1953.
52. Slottman, G. V., "Use of Oxygen in the Openhearth Bath", Iron Age, 159, No. 8, pp. 42-5, February 20, 1947.
53. Spedding, F. H., "Production of Rare Earth Metals", Industrial Engineering Chemistry, 44, p. 553, 1952.
54. Spedding, F. H., and Daane, A. H., "Preparation of Rare Earth Metals", Journal of Amer. Chemical Society, p. 2783, June 5, 1952.
55. St. Clair, H. W., "Refining Metals and Alloys by Filtration", U. S. Bureau of Mines, Report of Investigations, 4614, December, 1949.
56. Steinberg, M. A., Sibert, M. E., and Wainer, E., "Extractive Metallurgy of Zirconium by Electrolysis of Fused Salts", and "Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6 ", Electrochemical Society Journal, 101, pp. 63-78, February, 1954.
57. Stephens, W. W., and McClain, J. H., "Ductile Zirconium", Chemical Engineering, 58, No. 3, pp. 116-7, 1951.
58. Tanenbaum, M., Goss, A. J., and Pfann, W. G., "Purification of Antimony and Tin by a New Method of Zone Refining", Journal of Metals, pp. 762-3, June, 1954.
59. Taylor, J., "Ironmaking, Part V. Slag/Metal Reactions", Iron and Steel, 26, pp. 155-60, May, 1953.
60. Thews, E. R., "Melting and Refining Fluxes, Properties, Purposes and Effects of Modern Reducing Agents", Metal Industry, 73, pp. 511-14, December 24, 1948, and pp. 523-25, December 31, 1948.

SUPPLEMENTARY REFERENCE LIST

The following references were reviewed by abstract or title only, and are not cited in this report.

Process and Operational References:

Apfelbock, M., "The Smelting of the Principle Commercial Non-Ferrous Heavy Metals from the Standpoint of Modern Technology", Metallurgie u. Giesereitech, 3, pp. 235-8, 1954.

Axon, H. J., "Examination of Joules Work on the Metallurgy of Amalgams", Metallurgia, 47, pp. 27-8, January, 1953.

Bankloh, W., "Gases in Metals", Transactions, India Institute of Metals, 4, p. 231, 1950.

Brandau, O., and Tscham, G., "Refining with Pure Oxygen. Melting of Corrosion Resistant 18-8 Chromium-Nickel Cast Steel and Hydrogen Resisting Chromium-Molybdenum Cast Steel in the Basic Electric Arc Furnace by Refining with Gaseous Pure Oxygen", Metallurgie u. Giesereitech, 3, pp. 401-11, 1953.

Bryan, W. T., "Use of Oxygen in Melting Stainless Steel", Electric Furnace Steel Conference, Proceedings, Vol. 7, pp. 256-66, 1949.

Bucko, E., "Slag and Removal of Impurities in the Basic Open Hearth Furnace", Prace. Institute Ministerstwa Hutnic, 5, pp. 159-61, 1953.

Chaudron, G., "Problems of Metals of High Purity", Tech. Moderne, 37, pp. 137-45, and Chimie and Industrie, 56, p. 220, 1946.

Chaudron, G., "The Problem of Ultimate Traces of Impurities in Metals", Bulletin de la Societe Chimique de France, No. 4, pp. 419-22, April, 1954.

Chipman, J., "Activities in Liquid Metallic Solutions", Discussions, Farraday Society, No. 4, p. 23, 1948.

Crandall, W. B., and Lawrence, W. G., "Fundamental Properties of Metal-Ceramic Mix at High Temperature", U. S. Atomic Energy Commission, File No. NP-1705, July 31, 1950.

Cubiciotti, D. D., Dravnieks, A., and Blevitsky, R., "Reactions of Gases with Metals at High Temperatures", U. S. Atomic Energy Commission Publication No. NP-1003, P. 49, 1949.

Cubiciotti, D. D., "Solutions of Metals in Fused Salts", Journal of Metals, 5, No. 9, pp. 1106-8, September, 1953.

- Dautzenburg, Wilhelm, "Regarding the Refining of Metals by Intermetallic Reaction", Zeitschrift fur Erzbergbau und Metallhüttenwesen, 5, pp. 432-9, November, 1952.
- DuPont, B. T., and Fulton, R., "Five Ways to Make Iron Powder", Iron Age, 169, No. 17, p. 135, 1952.
- Eibmer, Goldenschmidt, and Vertes, "Preparation of Uranium Metal at the Cauchet Plant of the Atomic Energy Commission", Bulletin de la Societe Chimique de France, 1951.
- Ellingham, H. J. T., "Reducibility of Oxides and Sulfides in Metallurgical Process", Journal of Society Chemical Industry, 63, p. 125, 1944.
- Fast, J. D., Tuteign, A. I., and Overbasch, E., "Preparation and Casting of Metals and Alloys Under High Vacuum", Phillips Technical Review, 15, pp. 114-21, October, 1953.
- Fischer, R., "Refining of High Chromium Steel Heats in the Arc Furnace with Pure Oxygen", Stahleisen, 70, pp. 10-19, discussion pp 19-21, January 5, 1950.
- Flemming, H. W., "High Vacuum Metallurgy", Metallurgia, pp. 188-92, 1951.
- Flood, H., and Grjotheim, K., "Thermodynamic Calculations of Slag Equilibria", Journal of the Iron and Steel Institute, 171, p. 64, 1952.
- Fujita, E., "Production of Highly Pure Metallic Calcium by Thermal Reduction Method", Reports, Government Chemical Industrial Research Institute, Tokyo, 45, p. 378, 1950.
- Geach, G. A., and Summers-Smith, D., "Laboratory Arc Furnace for Melting Alloys Containing the Refractory Transition Metals", Metallurgia, 42, No. 250, pp. 153-6, 1950.
- Giesen, K., "Production and Uses of Purest Metals", Die Technik, 2, pp. 393-8, 1947.
- Hock, A. L., "Magnesium Extraction from Fused Salts", Magnesium Review and Abstracts, 9, pp. 1-30, December, 1953.
- Hughes, R. C., "Preparation of High Purity Lead", Electrochemical Society Journal, 101, pp. 267-70, June, 1954.
- Iandelli, A., and Ferro, R., "The Amalgams of Lanthanum", Atti. Accad. Nazl. Lincei Rend., Classe. Sci., Fis., Mat. e nat. 11, pp. 85-93, 1951.
- Jantsch, G., and Zemek, F., "The Separation of Chemically Pure Vanadium from the Gaseous Phase", Monatsh, 84, pp. 1119-26, 1953.

- Johnston, T. L., and Mahan, W. M., "Laramie Sponge-Iron Pilot Plant", U. S. Bureau of Mines, Reports of Investigations No. 4376, p. 44, 1948.
- Jenks, C. F., "Recovery of Usable Metal from Aluminum and Aluminum Alloy Drosses, Turnings, Swarf, etc.", Metallurgia, 33, pp. 302-3, 1946.
- Kroll, W. J., "Rare Metal Metallurgy - Special Production Methods for the Less Common Elements", Metal Industry, 73, pp. 263-5, 283-6, 307-8, 310, 323, 325, 1948.
- Kroll, W. J., Hergent, W. F., and Yerkes, L. A., "Improvements in Method for Reduction of Zirconium Chloride with Magnesium", Journal of Electrochemical Society, 97, p. 305, October, 1950.
- Kroll, W. J., "The Fused Salt Electrolysis for the Production of Metal Powders", Transactions Electrochemical Society, 87, pp. 551-68, 568-69, 1945.
- Lawrence, J. B., "Mercury, the Purest Metal", Instruments, 25, p. 310, 1952.
- Ludwig, Jr., J. N., "Use of Complex Deoxidizers", Electric Furnace Steel Proceedings, 6, pp. 208-12, discussion pp. 212-15, 1948.
- Lyon, P. W., Olson, C. M., and Lewis, E. D., "Preparation of Hyper-Pure Silicon", Journal of the Electrochemical Society, 96, pp. 359-63, December, 1949.
- Meister, G., "Production of Thorium, Zirconium, Uranium", Metal Progress, 53, pp. 515-20, 1948.
- Miller, G. L., "Metal Powders", Mechanical Engineering, 70, pp. 869-75, 1948.
- Montariol, F., Reich, R., Albert, P., and Chaudron, G., "Application of Zone Melting Technique to Obtain High Purity Aluminum", Comptes rendes, 238, No. 7, pp. 815-17, February, 1954.
- Nisbet, J. D., "Vacuum Melting Techniques", Iron Age, 161, pp. 79-82, 122, March 18, 1948.
- Oelsen, W., "Results of Research on Metal-Slag Reactions", Zeitschrift fur Erzbergbau und Metallhutenwesen, 1950.
- Pearsall, C. S., "Purification of Beryllium by Directional Crystallization", U. S. Atomic Energy Commission Technical Information Service, Oak Ridge, Tenn.
- Poland, F. F., "Distillation of Zinc and Refining of Residual Metals from Copper Base Alloys", Metals Technology, 13, No. 6, Amer. Institute of Mining and Metallurgical Engineers Technical Publication No. 2065, p. 15, 1946.

Pound, G. M., "Electrochemical Separations in Non-Aqueous Solutions", U. S. Atomic Energy Reports NYO-6010, Classified.

Powell, Lever, and Walpole, "Extraction and Refining of Germanium and Gallium", Journal of Applied Chemistry, 1, p. 541, 1951.

Quill, L. L., Editor, Chemistry and Metallurgy of Miscellaneous Materials ---Thermodynamics, McGraw-Hill, 1950.

Radzwicki, K., "Reclaiming Melts of High Speed Steel Waste in an Electric Arc Furnace", Prace Instytutow Ministerstwa Hutnictwa, 5, No. 3, pp. 113-18, 1953.

Regner, A., "Application of Thermodynamics for Solving Fundamental Problems of Metallurgical Processes", Hutnicke Listy, 7, p. 178, 1952.

Rogers, R. R., and Viens, G. E., "Refining of Magnesium by Vaporization at Extremely Low Pressure", Journal of the Electrochemical Society, 97, pp. 419-24, 1954.

Rossmann, M. G., and Yarwood, J., "The Use of Carbon Crucibles in Measurements on Rate of Evaporation of Liquid Metals in Vacuum", British Journal of Applied Physics, 5, p. 7, January, 1954.

Rugare, A. S., "The Metal Germanium and Its Use in the Electronics Industry", Metal Progress, p. 97, August, 1952.

Scheil, E., "Crystallization of Molten Metals", Giesserei, Tech. - Wiss. Beihefte, Metallkunde u. Giessereiw, No. 5, p. 201, 1951.

Schlechten, A. W., and Hanley, H. R., "In Metallurgy, the Accent is on New Metals, New Methods", Engineering and Mining Journal, p. 122, February, 1951.

Smatko, J. S., "Production of Some Rare Metals and Their Compounds, as Practiced by E. Merck Chemische Fabrik, Darmstadt", Office of M. G. for Germ. F. I. A. T. Final Report No. 783, NP-253, February 21, 1946.

Vickery, R. C., "The Vapor Phases of Metals", Metallurgia, 34, pp. 4-7, 1946.

Welch, A. J. E., "The Inorganic Chemicals of Some Metallurgical Processes", Annual Reports on Progress in Chemistry, 43, p. 129, 1947.

"Production of Pure Cerium by Electrolytic and Electrothermic Processes", Transactions of Institute of Mining and Metallurgy, 61, Part 4, p. 141, 1951-1952, Author not recorded.

"A Method for Preparation of High Purity Indium", Transactions of Institute of Mining and Metallurgy, 60, Part 3, p. 77, 1950-1951, Author not recorded.

"The Present State of Electrometallurgy of Non-Ferrous Metals", Zeitschrift fur Erzbergbau und Metallhüttenwesen, 5, p. 270, July, 1952, Author not recorded.

"Commercial Production of Sponge Iron", Iron Age, 163, No. 22, pp. 67-71, 82, 1949, Author not recorded.

"Behavior of Nobler Metals During Refining of Aluminum According to Triple-Layer Process", Zeitschrift fur Elektrochemie Bericht der Bunsengesellschaft fur Physikalische Chemie, 56, p. 1, January, 1952, Author not recorded.

"Facilitating the Reduction of Metal Compounds by Alloy Formation and Accompanying Calculations", Zeitschrift fur anorganische und Allgemeine Chemie, 266, p. 1, October, 1951, Author not recorded.

"Chemical Treatment of Molten Non-Ferrous Metals", Canadian Metals, 15, p. 32, May, 1952, Author not recorded.

"Direct Reduction of Fe Ores Using Fluidized Solids Technology", A. I. S. I. Preprint, 1951, Author not recorded.

"Advances in Extraction Metallurgy", Mining Journal, p. 97, May, 1952, Author not recorded.

Equipment and Materials References:

Busch, G., Huliger, F., and U. Winkler, "High Temperature-Pressure Furnace", Helvetica Physica Acta, 27, No. 1, pp. 74-80, 1954.

Cage, Jr., J. F., "Electromagnetic Pumps for High Temperature Liquid Metals", Mechanical Engineering, 75, pp. 467-71, 1953.

Chesnut, F. T., "How to Select Induction Heating Equipment", Steel, 24, pp. 109-12, 116, March 21, 1949.

Cross, H., and Simmons, W., "The Elevated Temperature Properties of Stainless Steel", A. S. T. M. Report on The Elevated Temperature Properties of Stainless Steel, Special Tech. Publication No. 124, 1952.

Gibaldo, F., "Rare Metals Require Precision Furnacing", Steel, p. 76, March 3, 1952.

Hartman, Irving, "Explosive Characteristics of Titanium, Zirconium, Uranium, Thorium, and Their Hydrides", U. S. Bureau of Mines, Report No. 4835, Amer. Society for Metals Review, 1952.

Hogel, Lennart, "Metallurgical Uses of High Frequency Furnaces in Sweden", Transactions of Fuel Econ. Conf., World Power Conf., Sect. C2, Paper No. 14, p. 11, 1947. (Preprint)

Jones, N. C., "A Note on Fused Stabilized Zirconia: A Modern High Temperature Refractory", Journal of the Institute of Fuel, 25, p. 66, 1952.

- Keith, W. P., "Design and Operation of Molybdenum-Wound, Hydrogen Atmospheric Furnace", American Ceramics Society Bulletin, 31, p. 76, 1952.
- McLain, S., "Materials for Nuclear Reactors", Chemical Engineering Progress, 50, pp. 240-44, May, 1954.
- Mikailson, B., "High Temperature Materials for Vacuum Service", Materials and Methods, 38, No. 6, pp. 110-15, 1953.
- Morse, Richard S., "High Vacuum Technology", Ind. Eng. Chem., 39, pp. 1064-71, 1947.
- Parker, E. R., "High Temperature Properties of Refractory Metals", Transactions of American Society for Metals, 42, pp. 399-404, 1950.
- Pearson, B. M., "Experiments on Forsterite Linings Reported Successful", Iron Age, 167, pp. 65-7, January 18, 1951.
- Planner, B. P., "Extremely High Temperature Materials", Western Metals, 10, No. 5, p. 43, 1952.
- Remmey, G. B., "Upper Useful Limits of Commercial Super-Refractories", American Ceramic Society Bulletin, 27, pp. 477-85, 1948.
- Rengstorff, and Fischer, "Cast Molybdenum of High Purification", Journal of Metals, 4, Transactions, p. 157, 1952.
- Schwartz, M. A., White, G. G., and Curtis, C. E., "Crucible Handbook: A Compilation of Data on Crucibles Used for Calcining, Sintering, Melting, Casting", U. S. Atomic Energy Commission, Technical Information Service, Oak Ridge, Tenn., ORNL-1354, p. 28, 1953.
- Shelton, S. M., "Invention of Possible Improvements in Production of Zirconium", Bureau of Mines Summary Report No. 7, NP-1394, February 14, 1950.
- Snyder, T., and Lipkin, D., "Topics on Vacuum Technique", National Nuclear Energy Series, Div. V, 3, Miscellaneous Physical and Chemical Techniques, p. 252, 1952.
- Stoddard, C. K., Mooz, W. E., "Observations on Design and Operation of High Vacuum Systems", Chemical Engineering Progress, 49, No. 4, pp. 197-202, April, 1953.
- Taub, J. M., and Doll, D. T., "A New Design Vacuum-Melting Furnace", U. S. Atomic Energy Commission Unclassified Report, LAMS-1130, p. 24, 1950.
- Tice, E. A., "Preserving What You Have. From the Corrosion Engineer's Viewpoint", Chemical Engineering Progress, 48, p. 329, 1952.

Trombe, F., "Super-Refractory Oxides", Bulletin Soc. France Ceramics, No. 3, p. 18, 1949. Also, Research, 1, p. 393, 1948.

Whittemore, O. J., and Marshall, D. W., "Fused Stabilized Zirconia Refractory", Journal of American Ceramic Society, 35, p. 85, 1952.

Williams, A. F., "Refractory Concrete", Engineer, 187, pp. 496-8, May 6, 1949.

Yamagnchi, T., "Melting and Casting of Nickel Alloys with Special Reference to Melting of Nichrome in a High Frequency Induction Furnace", Kinzoku, 21, No. 1, p. 33, 1951.

"New Zirconia Useful at Temperatures to 4600° F.", Materials and Methods, 33, p. 81, March, 1951, Author not recorded.

Patent References:

Anglo-American Corporation of South Africa, Ltd., "Metal Distillation and Recovery", British Pat. 660,688, November 14, 1951.

Balbhausen, Carl, to Deutsche Edelstahlwerke A. - G., "Atomizer for Metallic and Non-Metallic Substances", German Pat. 811,899, August 23, 1951.

Bancroft, G. H., "Vacuum Coating Apparatus", U. S. Pat. 2,584,660, February 5, 1952.

Bleloch, W., "Smelting of Metallic Oxides in Blast Furnace", British Pat. 668,218, March 12, 1952.

Breyer, Frank G., to Dominion Magnesium, Ltd., "Multiple Retort Still for Metals", U. S. Pat. 2,386,429, October 9, 1945.

Burkhardt, G. R., "Treatment of Metals with Noble Gases", U. S. Pat. 2,426,814, September 2, 1947.

Chilean Sales Corporation, "High Purity Titanium", British Pat. 698,233, 698,234, 698,235, 698,236, 1954.

Cuscoleca, O., Grohs, F., Rosner, K., Kuhnelt, W., to Osterreichisch-Alpine Montanges, Austrian Pat. 178,101, April 10, 1954.

Dobrin, H., to Furn. Eng., Inc., "Melting Pan in Refractory Metal Melting Furnaces", U. S. Pat. 2,414,860, January 28, 1947.

Doucot, R., to Compagnie des freins and signaux Westinghouse, "Retort for Distillation of Selenium, etc.", U. S. Pat. 2,654,700, October 6, 1953.

Dunlap, Jr., W. C., to General Electric, "Germanium Pellets", U. S. Pat. 2,595,780, May 6, 1952.

Erasmus, H. D. W., "Purification of Ferrochromium", U. S. Pat. 2,473,020 and 2,473,021, June 14, 1949.

Fischer, E., "Vaporizer for Thermally Evaporating Aluminum and Similar High Boiling Materials", German Pat. 802,304, February 8, 1951.

Fruhirth, O., to Donan Chemie A. - G., "Production of Metals from Halide Compounds", Austrian Pat. 169,067, October 10, 1951.

Gjedebo, F., "Separating Metals", U. S. Pat. 2,468,660, April 26, 1949.

Glaser, K., "Purification of Metals and Alloys", Austrian Pat. 166,453, August 10, 1950.

Goebel, F., to Treibacher Chemische A. - G., "Metals by the Thermite Process", Austrian Pat. 169,315, November 11, 1951.

Gohr, E. J., and Tyson, C. W., "Apparatus for Contact Reactions of Fluidized Solids with Gases", U. S. Pat. 2,470,395, May 17, 1949.

Gross, P., "Distillation of Nonvolatile Metals", British Pat. 666,869, February 20, 1952.

Hansgirg, F. J., "Magnesium", U. S. Pat. 2,582,119 and U. S. Pat. 2,582,120, January 8, 1952.

Hansgirg, F. J., "Continuous Process for Recovery of Magnesium", U. S. Pat. 2,570,232, October 9, 1951.

Hansgirg, F. J., "Vacuum Still for Metals", U. S. Pat. 2,391,156, 1946.

Hybinette, I. E., and Cary, F. C., "Thermal Production of Magnesium and Other Metals", U. S. Pat. 2,396,658, March 19, 1946.

Johannsen, K., "Roughening the Surface of Metal Articles with Simultaneous Removal of Undesired Impurities", German Pat. 803,739, April 9, 1951.

Jordon, J. F., "Extraction of Tin from Iron Alloys", U. S. Pat. 2,474,979, July 5, 1949.

Jordon, J. F., "Metal-Refining Tower for Countercurrent Contact of Immiscible Metallic Liquids", U. S. Pat. 2,572,489, October 23, 1951.

Jordon, J. F., "Vapor Phase Smelting Process", U. S. Pat. 2,667,413, January 26, 1954.

Kroll, W. J., "Melting Hafnium, Zirconium, Titanium", U. S. Pat. 2,548,897, April 17, 1951.

Lark-Horovitz, K., and Whaley, R., "Rectifier Alloys", U. S. Pat. 2,588,253, March 4, 1952.

Nisbet, J. D., "Alloys", U. S. Pat. 2,564,498, August 14, 1951.

Platon, J. G., "Refining of Oxidized Steels and Manufacture of Alloy Steels", British Pat. 656,396, August 22, 1951.

Pontzen, H., and Eykelen, H., "Process and Melting Furnace for Separating Metals Not Alloyed Together, Especially of Scrap Light Metal", German Pat. 805,087, May 7, 1951.

Quinn, J. P., "Purification of Titanium", British Pat. 697,487, September 30, 1953.

Regie nationale des usines Renault, "Reduction Furnace for the Reduction of Metallic Compounds such as Tungsten Oxides, by the Use of Reducing Gases to Produce Metal Powders", German Pat. 822,441, 1954.

Reid, A. F., "Apparatus for Fractional Sublimation", U. S. Pat. 2,628,892, 1953.

Ruthner, O., "Separation of Metals in Powder Form from their Salt Solutions", U. S. Pat. 2,657,989, November 3, 1953.

Schlichten, A. W., Kroll, W. J., and Yerkes, L. A., "Distillation Apparatus for Recovery of Zirconium", U. S. Pat. 2,482,127, September 20, 1949.

Schoenlaub, R. A., "Recovery of Metallic Oxides such as Zirconia", U. S. Pat. 2,578,748, December 18, 1951.

Smalley, O., "Incorporation of Additives into Molten Metal", U. S. Pat. 2,574,764, November 13, 1951.

Stern, M., "Low Carbon Nickel-Iron Alloys and Nickel Steels", British Pat. 571,593, August 31, 1945.

Unger, C. E., to American Foundry Equipment Company, "Metal Pellets (Method of Production from Melt)", U. S. Pat. 2,398,455, April 17, 1948.

van Hoorn, A., and Thurmer, G., "Arrangement for the Evaporation of Metals and Electron Tube Equipped with It", German Pat. 804,747, April 30, 1951.

Vdy, M. J., "Metallurgy", U. S. Pat. 2,582,469, January 15, 1952.

Whitney, Jr., L. T., "Refining Ferrous Metals", U. S. Pat. 2,669,511, February 16, 1954.

Winter, Jr., C. H., to DuPont, "Reduction of Titanium and Zirconium", U. S. Pat. 2,607,674, August 19, 1952.

"Centrifuge for Separating Molten Metal from Slag", U. S. Pat. 2,415,210, February 4, 1947, inventor not recorded.

"Apparatus for Separating at Least One Component from a Liquid Mixture by Distillation", German Pat. 807,813, July 5, 1951, inventor not recorded.

