1950

Preparation of zirconium metal

Kenneth Albert Walsh
Iowa State College

NOTE TO USERS

93

PREPARATION OF ZIRCONIUM METAL

by

Kenneth Albert Walsh

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1950

TABLE OF CONTENTS

I. INTRODUCTION

The combination of nuclear and physical properties possessed by zirconium makes it a valuable material for use in the construction of nuclear reactors. For thermal neutrons, the absorption cross section of zirconium may be about 0.20 barns (1). This absorption cross section is less than columbium and steel, only twice that of aluminum, but forty times that of beryllium (2). The high resistance to corrosive attack by specific agents makes it useful for heat transfer surfaces in contact with pile coolants. These properties, in addition to the favorable features of strength, ductility and malleability, encouraged development of methods for the production of pure zirconium metal which would be more economical and more readily expanded to a large scale operation than processes currently in use.

Hafnium, which occurs in the ore and has similar chemical properties, is present in all commercial zirconium produced by methods currently in use. The hafnium content ranges from one to three per cent for zirconium produced in the United States. The absorption cross section of hafnium is about 101 barns for thermal neutrons (3). Prior separation of hafnium from the zirconium before using the metal in nuclear reactors is obviously necessary. At the Ames Laboratory of the Atomic Energy Commission the hafnium is removed by passing a methanol solution of zirconium tetrachloride through a column packed with activated silica gel which preferentially adsorbs the hafnium (4). The effluent from these columns must be treated to remove all other

impurities which would increase the effective neutron cross section or impair the corrosion resistance of the metallic zirconium.

The treatment of the hafnium-free material must include the preparation of necessary intermediate and final compounds to be used in the reduction process. The reduction to zirconium metal by the sealed bomb method affords ample opportunity for expansion in productive capacity.

It was assumed that the elimination of hafnium would not have any large effect on the properties of zirconium or its compounds. The unit processes in the preparation of zirconium metal could be developed without prior separation of hafnium. Application of these processes to the hafnium-free material could then be made without major modifications.

II. REVIEW OF THE LITERATURE

Berzelius (5) in 1824 reduced potassium-zirconium fluoride with sodium and obtained for the first time a zirconium powder, probably mostly lower oxide. Troost (5) employed the method of reducing gaseous zirconium tetrachloride with magnesium or sodium and the reduction of sodium fluozirconate with aluminum in 1865. Neither Berzelius nor Troost made a pure metal that displayed malleability and corrosion resistance.

In 1914 Lely and Hamburger (6) obtained a ductile zirconium through the reaction of zirconium chloride with sodium in a sealed pressure bomb. By careful control of the temperature gradient and rates of formation zirconium tetrachloride was made by treating zirconium oxide with chlorine saturated with carbon tetrachloride. The zirconium chloride was a compact dense material which did not react readily with atmospheric moisture. A mixture of the zirconium chloride and sodium was placed in the bomb between layers of sodium. The sealed bomb was heated to initiate the reaction. Coarse metallic pellets of zirconium in the product were separated by washing with concentrated hydrochloric acid or concentrated nitric acid. Finally the metal was washed and dried with organic solvents. The pellets could be pressed into a rod or melted in an electric vacuum furnace to give a compact metal which was practically pure, very ductile, and resistant to attack by acids and alkalies.

By thermal decomposition of zirconium tetraiodide on a heated

filament de Boer and Fast (7) first prepared zirconium in the massive form as rods in 1926. The powdered or lump zirconium, prepared by other reduction schemes, is introduced into a Pyrex glass chamber equipped with electrodes to which a hairpin filament can be connected. The filaments, on which the crystalline zirconium rods form, are made of tungsten or zirconium wire. After placing the crude zirconium in the vessel, the system is degassed by vacuum heating to a pressure of 0.0001 mm. of mercury. Iodine is then admitted from a side arm on the unit. The hairpin filament is heated to 1300-1450 degrees centigrade by electrical resistance and the crude zirconium is warmed to about 300 degrees centigrade. At about 100 degrees centigrade the iodine combines with the zirconium to form zirconium tetraiodide, which acts as a carrier. At 150 degrees centigrade the partial pressure of zirconium tetraiodide is approximately 0.0001 mm. of mercury and it rises sharply to a maximum at about 250 degrees centigrade. Above this temperature the vapor pressure ceases to rise as zirconium tetraiodide begins to react with the excess zirconium to form non-volatile zirconium triiodide and at still higher temperatures zirconium diiodide. As a result of the equilibria existing between zirconium tetra-, tri-, and di-iodide the rate of formation of ductile zirconium does not increase appreciably above 250 degrees centigrade and above 350 degrees centigrade it finally begins to decrease again. The tetraiodide decomposes on the hot filament depositing zirconium. The crude metal is freed from oxides, nitrides, carbon and carbides, which remain behind. Many elements are attacked by iodine and, if they form a volatile iodide,

may be deposited with the zirconium. Aluminum, silicon, boron, iron and titanium can not be removed from zirconium by this method. The iodide decomposition method is limited by the source of electrical current available, since a rod of zirconium approximately 1/4 inch round requires a current of 100-200 amperes for resistance heating to maintain the proper temperature. Heat dissipation becomes a problem with thick wires and heavy currents as the reaction product accumulates. The Foote Mineral Company produces zirconium commercially by the iodide method.

The production of less pure zirconium by reduction of zirconium tetrachloride vapor with molten magnesium in a helium atmosphere has been described by Kroll (8,9,10). Zircon sand, which is used as the starting material, is converted to zirconium carbide by fusing a mixture of zircon and graphite in an arc or resistance furnace. Through the reaction with chlorine at elevated temperatures a crude zirconium chloride is obtained from the carbide. Silicon chloride is removed by using a condenser heated to 100 degrees centigrade for deposition of the zirconium chloride. Purification of the chloride is accomplished by sublimation in a hydrogen atmosphere, which removes oxides, carbon and carbides, and iron. In the reduction step the zirconium tetrachloride is sublimated to react with molten magnesium in a helium atmosphere forming lump zirconium and magnesium chloride. The excess magnesium and magnesium chloride are removed by vacuum distillation at 885 degrees centigrade. The zirconium sponge is conditioned with mixtures of air and helium to minimize the fire hazard when the sponge

is removed from the retort. The sponge is compressed into briquets which are melted in a graphite crucible in a vacuum or inert atmosphere in induction or split-graphite resistance furnaces. Such metal is often referred to as Bureau of Mines zirconium.

The Bureau of Mines method can be expanded to meet an increased demand for zirconium metal more readily than the iodide decomposition process. This metal does not show the corrosion resistance exhibited by iodide metal (1), probably as a result of the increase in carbon and iron contamination of the metal. The method requires the preservation of a completely moisture-free atmosphere with operations involving solid or gaseous zirconium tetrachloride. The fire hazard associated with the zirconium sponge is also a serious problem.

Lilliendahl and co-workers (11) at Westinghouse have produced relatively pure zirconium powder by reducing the oxide with mixtures of magnesium and magnesium chloride or calcium and calcium chloride. The charge is heated by induction to 1000-1200 degrees centigrade in an argon atmosphere. A molybdenum crucible within the graphite heater is used as container for the charge. The unit is located in a Vycor tube. The vaporization of magnesium or calcium is suppressed by the inert gas filling. The powdered metal obtained is compressed into compacts and sintered in high vacuum. The resulting metal is less ductile and is harder than that from the other processes, but it can be drilled, tapped and machined.

Fusion electrolysis of double fluorides and double chlorides has been attempted (5). Oxide was added to avoid anode effect. This

gave a product which contained some oxygen in solid solution. The metallic product was frequently obtained as finely divided or colloidal particles. Electrolysis of an aqueous solution of zirconyl sulfate was most successful for the electrowinning of zirconium from aqueous media. The great chemical reactivity of such zirconium and the stability of the zirconyl ion offer little hope for electrolytic methods with aqueous solutions, since the lower oxide will most generally be formed.

The physical and chemical properties of metallic zirconium are markedly changed by the presence of small amounts of certain impurities. These effects stress the importance of producing zirconium metal of extremely high purity. The reaction between zirconium and atmospheric gases at elevated temperatures forms solid solutions. Fast (12) reported that zirconium dissolves up to forty atomic per cent oxygen without the appearance of the zirconium oxide phase. Nitrogen also forms solid solutions with the metal. The presence of these gases in solid solution with zirconium makes the metal brittle in the cold state. Zirconium containing oxygen in excess of 0.2 per cent by weight can no longer be cold rolled and shows a marked increase in hardness according to Lilliendahl (13). The hardness of zirconium metal has sometimes been used as a measure of the oxygen content of the metal.

Zirconium metal to be used in nuclear reactors must be of very high purity. Substances which increase the hardness too much must be excluded. In addition the metal must not contain impurities which

increase the absorption of neutrons or increase the rate of corrosion. In general, metal of sufficient purity to withstand the corrosion test will exhibit adequate nuclear properties, although this eliminates possibilities of improving corrosion resistance by alloying with certain elements. The specific test (1) for corrosion resistance of zirconium metal consists of immersion in deaerated water heated to 315 degrees centigrade in a sealed bomb. The change in weight,

Table I

Analysis of Non-Corrosive Zirconium

Element	p.p.m.	Element	p.p.m.
Fe	300	C	500
Ti	100	O	1000
Al	150	Si	70
N	70	Ca	<100

expressed in milligrams per square centimeter per month, is taken as a measure of the corrosion resistance. These conditions of the test approximate the conditions within the nuclear reactor with water cooling and the service conditions to be expected of the zirconium metal. Much of the zirconium metal now produced does not show sufficient corrosion resistance. The difference in corrosion properties between samples is attributed to the presence of certain impurities. The

analysis of zirconium metal which did not corrode in the high temperature water is shown in Table I for the major impurities which are most difficult to eliminate (1).

The purity of a zirconium product depends on elimination of the contaminants and excluding these materials in all subsequent operations. Although numerous methods are reported for the formation of pure zirconium compounds, many are prohibited in process development by the cost and unavailability of large supplies of rare chemical reagents, which restrict these methods to use in laboratory or analytical procedures. The difficulties encountered in handling certain precipitates on large scale, the problems associated with the recovery of costly materials, or the formation of compounds which are not useful intermediates in the zirconium process eliminates many other purification schemes.

Among the methods which could be considered in process development is the purification of aqueous solutions of zirconium in nitric acid by ion-exchange with Amberlite IR-100, which was demonstrated by J. A. Ayres (14). The dilute solutions employed would entail long periods of time for ion-exchange column operation for the required scale of zirconium production. The large volumes of solutions would increase the cost of concentration or filtration operations in succeeding stages of the process.

The sublimation of zirconium tetrachloride in a hydrogen atmosphere is employed in the process of the Bureau of Mines (10). The iron found as ferric chloride in the zirconium chloride is reduced to

ferrous chloride which remains behind. Chromium is likewise removed as chromous chloride. The condensing surface is kept above 100 degrees centigrade to give a dense form of zirconium tetrachloride and to reduce contamination by the more volatile silicon tetrachloride. The introduction of impurities by carrying in the gas stream of zirconium tetrachloride during the sublimation limits the degree of purity which can be obtained.

The precipitate of zirconium salicylate formed by the addition of a solution of ammonium salicylate to aqueous zirconyl chloride is soluble in dilute ammonium hydroxide (15). The insoluble hydroxides or hydrous oxides, such as aluminum and iron, can be removed by filtration. Acidification with hydrochloric acid reprecipitates the zirconium salicylate, which can be ignited to a pure zirconium oxide.

Numerous applications of the formation of zirconyl chloride crystals in separations and purifications of zirconium have been reported (16,17, 18). Zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, is readily soluble in hot hydrochloric acid. At a concentration of hydrogen chloride of 318 grams per liter, zirconyl chloride is least soluble at room temperature (17). The decrease in solubility of zirconyl chloride with the addition of hydrochloric acid to aqueous solutions of zirconyl chloride or the change in solubility of zirconyl chloride with temperature has been used for the separation of crystalline zirconyl chloride in the pure state. After filtration the zirconyl chloride crystals have been washed with hydrochloric acid. The condition of high acid concentration

in heated solutions requires the use of special equipment in the concentration and crystallization steps of the method. Filtration and washing of the zirconyl chloride crystals must also avoid further contamination of the product.

III. THEORETICAL AND GENERAL CONSIDERATIONS

The formation of a metallic product in the massive form by the sealed bomb technique is based on the use of an exothermic chemical reduction capable of generating enough heat to bring the reaction products to the molten condition. The reaction must proceed rapidly to overcome heat losses from the bomb. While the reaction products are in the liquid state, separation into slag and metallic phases will occur, if the phases are immiscible and have sufficient difference in density. This method for the production of metals differs from a similar method in which the reaction products are heated by external sources to the melting point to accomplish a separation of phases. The following discussion pertains to the process in which the fusion of the reaction products results from the exothermic heat of the reaction.

Among the methods which are used to facilitate the separation of phases is the addition of fluxing agents. These do not enter the chemical reaction, but are used to lower the melting point of the slag phase. Calcium chloride and sodium chloride are examples of fluxing agents which are added to increase the yield of the metal product.

The addition of other metals to the reaction charge is employed to lower the melting point of the metallic phase. In this way the high melting metals can frequently be recovered as massive metal. The elimination of leaching processes for the recovery of a metallic

powder from the reaction products is a distinct advantage.

In the case of reversible reactions an alloying addition may reduce the activity of the metallic product so the equilibrium is shifted to give a more favorable recovery of the metal. This is analogous to the use of a mercury cathode in electrolytic processes which reduces the activity of the metallic product by forming an amalgam.

The addition of a large quantity of a second metal as a collecting agent is sometimes used in the case of rare metals. Recovery of the rare metal from the massive alloy is made in subsequent operations.

In some cases the primary reaction forming the desired metal product is not sufficiently exothermic to provide the necessary increase in temperature to fuse the reaction products. The heat evolution can be supplemented by auxiliary reactions, so-called "booster" reactions, to create the heat effect required for the fusion and separation of the insoluble phases. Occasionally the booster reaction is utilized to raise the temperature of the primary reactants to initiate the primary reaction.

In addition to the thermal effect produced by the secondary reaction, the booster reaction may become an important factor in the formation of massive metal as a result of the action of the products of this reaction. The product of the booster reaction may facilitate the separation of phases by lowering the melting point of the slag. For example, the use of iodine as the booster reagent for a primary reduction of a metal fluoride will produce an iodide

which will lower the melting point of the fluoride slag. In other supplementary reactions a metal product may lower the freezing point of the primary metal product by forming an alloy with it. Other booster reactions may accomplish both of these effects. For example, the use of a metal iodide as the booster reagent in a fluoride reduction may be used to lower the melting point of the fluoride slag and to decrease the temperature of fusion of the metallic phase through the formation of an alloy.

Combinations of the different additions to the reaction charge can be employed. By proper fluxing of the reaction products and the addition of an alloying metal, the use of a thermal booster may be eliminated. Similarly, an alloying addition may be combined with the addition of a thermal booster to obtain the maximum yield of the desired metallic product.

The formation of alloys for the study of constitutional diagrams by the sealed bomb method is a valuable tool in metallurgical research. The alloys may be prepared by the simultaneous reduction of compounds of the constituent metals. The other constituents of the alloy system may be added to the reaction charge as the pure metal. Addition of the alloying metals as booster reagents may also facilitate the preparation of the desired alloys.

The formation of a pure metallic product by the bomb reduction process requires the exclusion of undesirable materials which cannot be removed in a subsequent remelting or casting operation. This includes the effects of impurities in the components of the bomb charge

which would give unfavorable additions to the metal. The distribution of an impurity between the slag and metallic phase may reduce the undesirable aspects of certain types of impurities. Thus, the presence of calcium chloride in a metal chloride to be reduced by calcium would not be harmful.

Undesirable additions of fluxing agents or alloying agents must be avoided. A reaction between the reducing agent or the metallic product and the fluxing reagent may introduce impurities. Consequently, such additions are usually made in the form of highly stable compounds or as a compound of the reducing agent other than that formed in the principal reaction. Unless an alloying addition of a permanent nature is intended, the metallic addition should be one which can be subsequently removed by chemical or physical methods.

Reagents which are added to supplement the heat of reaction may be a source of contamination of the metal. This may occur if the metal products form stable compounds with the booster reagent which enter the metallic phase of the reaction products.

Metallic impurities may alloy with the metallic phase to give an undesirable distribution between the slag and metallic phases. The reducing agent may also alloy to some extent with the product to give a permanent addition of an undesirable nature.

The compound which is reduced in the principal reaction may include compounds which are impurities. If these impurities are also reduced by the reducing agent, the metallic product may become impure. Solid solutions may also form between the metal product

and certain types of impurities in the starting material, notably oxide contamination. Any impurities in the starting materials which would be a source of contamination of the metal must be removed in purification processes preceding the reduction, if they can not be removed in a final operation by chemical treatment or melting.

Another source of contamination of the metal results from the reaction with the surroundings. This contamination results from the reaction at the elevated temperature of the charge or the products with the bomb walls or the refractory liner often used in the reduction. The instantaneous development of heat by a rapid chemical reaction in the bomb decreases the time during which reactions of this type may act to introduce impurities.

The exclusion of atmospheric effects in chemical reactions producing a metal is often very important. The presence of oxide films may prevent coagulation of the metal droplets into a massive piece of metal. In other cases the effect of oxide may detract from the ductility of the metal. The sealed bomb is ideally suited for the isolation of the reaction mixture from the atmosphere. Control over atmospheric effects must still be exercised during the preparation of the starting materials and the preparation of the reduction charge.

The selection of a compound of the metal to be prepared is based on a few fundamental considerations. Since the reaction occurs in a sealed bomb, the generation of extreme pressures at the elevated temperatures must be avoided. Compounds which form gaseous products must be excluded from the possible choices. This eliminates the use

of hydrides, ammonium compounds, nitrates and hydrated compounds. The heat of reaction with the reducing agent should not be so great that extreme temperatures are reached. This may create undue pressures by vaporization of the metal product or increase the difficulty in the insulation of the bomb wall from the temperatures developed in the reaction mixture. Sulfates, chlorates, and similar salts of oxygen acids generally give too exothermic a reaction with the reducing agent to be useful.

The products formed in the reduction should not result in the formation of a high melting slag from which separation of the metallic phase is hindered. The non-metallic slag should not react with part of the starting material or with the final product. For example, a reduction of an amphoteric oxide with sodium may result in the formation of a salt between sodium oxide and the amphoteric oxide. Solid solutions of an oxide slag in the metal product may alter the physical properties of the metal.

The choice of the compound to be used as a starting material in the reduction may be governed by the degree of purity expected in the preparation of that compound. Hygroscopic materials may introduce oxide in the metal or develop excessive pressures when the water forms gaseous products in the bomb. Consideration of the economic aspects of the preparation of the compound for commercial development of the process is an important factor.

In the sealed bomb reduction of compounds to the metal the compounds most generally employed are the oxides, sulfides, halides

and double halides with the alkali metals. The bromides and iodides are frequently too hygroscopic and the low percentage of the metal in the compound is a disadvantage. The use of bromides or iodides requires the installation of equipment to recover the halogen from the slag for recycling in the process. This economic factor is also a disadvantage associated with the reduction of bromides or iodides.

The free energy change associated with the reaction between the compound of the metal to be prepared and the reducing agent partially determines the available materials for use in the reduction charge. Data are generally not available for the free energy of formation of compounds at the temperatures of the reaction. A useful empirical relationship is available in the standard electromotive force values for aqueous solutions. The metals lowest in the series are generally produced by more economical methods than the bomb method. The metals generally produced by a bomb reduction usually lie in the region between zinc and aluminum in the series. The choice of a reducing agent for the preparation of these metals in a bomb reduction is limited to those materials which will furnish a favorable change in free energy in the reduction reaction. For the reduction to metals which lie in the region between zinc and aluminum in the electromotive force series, the available reducing agents include the alkali and alkaline earth metals, magnesium, and aluminum.

In the development of a commercial process for the production of a metal by bomb reduction methods, the economic factors govern the choice among useful reducing agents. This usually limits the metallic

reducing agents to calcium, sodium, magnesium and aluminum. Another aspect is the purity attained with the use of commercially available supplies of the reducing agent.

The properties of the slag formed in the reduction process influence the choice of the reducing agent. The melting point of the slag may be too great for rapid separation of the reaction products into the insoluble phases. The stability of the compound formed with the reducing agent is important, if it dissociates into gaseous products at the elevated temperatures. The formation of magnesium sulfide slag is to be avoided if the temperature reached in the bomb promotes dissociation into magnesium and sulfur vapors.

The booster reagent selected must give the necessary increase in heat evolution to fuse the reaction products, if one is required. The additional effects which facilitate the separation and increase the yield of metal in the primary reaction may be another factor in the choice of the booster reagent. In general, the booster reagent combines with the same reducing agent as is used in the primary reaction unless the main charge is segregated from the booster charge. The purity of available booster reagents and the influence they may have on the purity of the final product are important.

Boosters used primarily for the thermal effect are potassium chlorate or various sulfates. These serve no other purpose because the molar quantities required are negligible compared to the main charge. Iodine and sulfur are examples of booster reagents which may also lower the melting point of the slag. Supplementary reactions

which serve to lower the melting point of the metal are less commonly used. The addition of zinc fluoride to improve the reduction yield of a fluoride may accomplish this purpose by alloying the metal with zinc. In this case the addition may not be deleterious, if the zinc fluoride is pure, since zinc metal may be volatilized during the remelting operations. Zinc chloride booster with a fluoride charge will serve the dual role of lowering the melting point of both phases in addition to the thermal effect.

The bomb assembly used in the reduction must protect the reaction materials and products from the atmosphere at the high temperatures developed by the reaction. Since the bomb reaches an elevated temperature it must be strong enough to withstand normal increases in pressure within the bomb. These requirements are usually obtained with a steel bomb closed at one end. The closure at the other end is maintained with an ordinary pipe cap or by the use of a gasketed cover plate. The slag covering the metal product also protects it from atmospheric effects by enclosing the liquid metal in a refractory envelope.

Interaction between the contents of the bomb and the bomb walls may be eliminated by lining the bomb with a suitable refractory material. This is important if the metal product has a strong tendency to form alloys with the iron. With a refractory liner the bomb supplies the mechanical strength needed to retain the material and the refractory prevents iron contamination of the product.

Many variations are possible in the method of locating the charge

within the bomb or its refractory liner. The charge with the booster may be thoroughly mixed and placed in the bomb. Modifications include the segregation of the booster charge from the main charge. Lining the inside of the bomb with the booster charge may protect the bomb from the main products and serve as the refractory liner. For the reduction of volatile compounds the reducing agent may be packed completely around the compound so the reduction occurs between a gaseous compound and the solid reducing agent.

Naturally, the charge to be located in the bomb must be stable at room temperature or this operation would be too hazardous. Once the charge is in the bomb and the closure has been made the reaction is initiated by heating the bomb. The temperature of the pit in which the bomb is placed is a variable which may be extremely important in improving the yield of metal obtained. As a general rule the larger the bomb, the lower the temperature maintained in the pit.

There are other factors in the successful application of the bomb reduction method to the preparation of metals. Most of these must be determined experimentally. The effect of particle size of the materials comprising the charge cannot be satisfactorily predicted. As the size of the bomb is increased, minor variations in the particle size of reactants become less important.

The composition of the refractory liner is dependent upon the chemical properties of the materials in the charge and the substances formed in the reduction. The choice of a refractory material depends upon the experimental results obtained with each material. This

choice is most generally made on the basis of the interaction with the reaction mixture and the undesirable impurities which become associated with the metal product.

IV. MATERIALS AND EQUIPMENT

The availability of zirconium tetrachloride made possible the separation of the zirconium development program into three stages, each using the chloride as the starting material. In the first step, studies were made on the removal of impurities from the methanol solution of zirconium tetrachloride or the residue obtained from the methanol recovery. The second phase of the investigation required the preparation of intermediate materials to be used directly or indirectly in the reduction process. The final stage was the reduction of a suitable zirconium compound to metallic zirconium.

The volumes of zirconium solutions to be treated are decreased by the great solubility of zirconium tetrachloride in alcohol and water. The reactivity with water is disadvantageous if the solid zirconium tetrachloride is used, because it exhibits a strong tendency to hydrolyze on contact with atmospheric moisture. Although the material is quite pure by comparison with other commercial zirconium salts, the impurities in zirconium tetrachloride would contaminate the metal product to a high degree. The analyses of four drums of zirconium tetrachloride from the Titanium Alloy Manufacturing Company are included in Table II to show the order of magnitude of the purification problem.

The preparation of pure zirconyl chloride by crystallization from acidic solutions used reagent grade concentrated hydrochloric acid in the formation of the mother liquor of the desired concentration. After

the filtration the crystals of zirconyl chloride were washed with C. P. acetone, which was helpful in reducing the concentration of iron and titanium salts.

Because of the high acidity of the solutions involved in the formation of pure zirconyl chloride, a glass-lined evaporator equipped with

Table II

Analysis of Commercial Zirconium Tetrachloride

Drum No.	Fe, p.p.m.	Ti, p.p.m.	Hf, %
554	650	55	1.95
555	935	60	2.15
556	850	200	2.15
588	1000	55	2.20

a steam jacket was used for concentration of solutions and crystallization of the solid. The evaporator had a capacity of thirty liters of boiling solution. The mother liquor containing the crystallized zirconyl chloride was vacuum filtered on size 6 Buechner funnels. In expanded scale of operations filtration with a centrifuge is anticipated.

The conversion of zirconyl chloride to zirconium oxide was obtained by ignition in quartz tubes closed at one end. These tubes were 9 inches in diameter and 40 inches long. Ten to twelve pounds of zirconium oxide were formed from one batch of zirconyl chloride. The tubes

were heated in the pit of a gas-fired furnace. The evolved water vapor and hydrogen chloride were drawn through a water-cooled condenser to the receiver by a water aspirator. Further ignition at higher temperatures in a smaller furnace was completed in quartz tubes 6 inches in diameter and 24 inches long. Approximately six pounds of zirconium oxide were treated in each batch.

Zirconium compounds which can be used for the reduction process include zirconium tetrachloride, zirconium tetrafluoride, and the double fluorides with the alkali metals. Zirconium oxide was less promising because of the possible formation of solid solutions of zirconium oxide in the metal.

Zirconium oxide obtained by the ignition of zirconyl chloride can be converted to zirconium tetrachloride by treatment with chlorine and carbon tetrachloride in a manner similar to that used by Lely and Hamburger (6). Therefore, zirconium tetrachloride, as received, was used to test the value of this compound in the reduction process.

Potassium fluozirconate, K_2ZrF_6, was obtained from Beryllium Corporation of America for preliminary studies of the reduction process. It was also obtained by treating zirconium tetrafluoride with a solution of reagent grade potassium fluoride on a laboratory scale in Pyrex beakers. The presence of fluoride ion caused some etching of the glassware, but the small quantities of silicon introduced did not affect the results in the experimental reductions.

Zirconium tetrafluoride is a highly desirable compound for use in the bomb reduction to give zirconium metal. The material is more inert to attack by atmospheric moisture than the tetrachloride, which eases the difficulty in handling the solid material. The increased heat of reaction between the fluoride and the reducing agents over other compounds makes a valuable contribution in raising the temperature of the reaction products above the melting point.

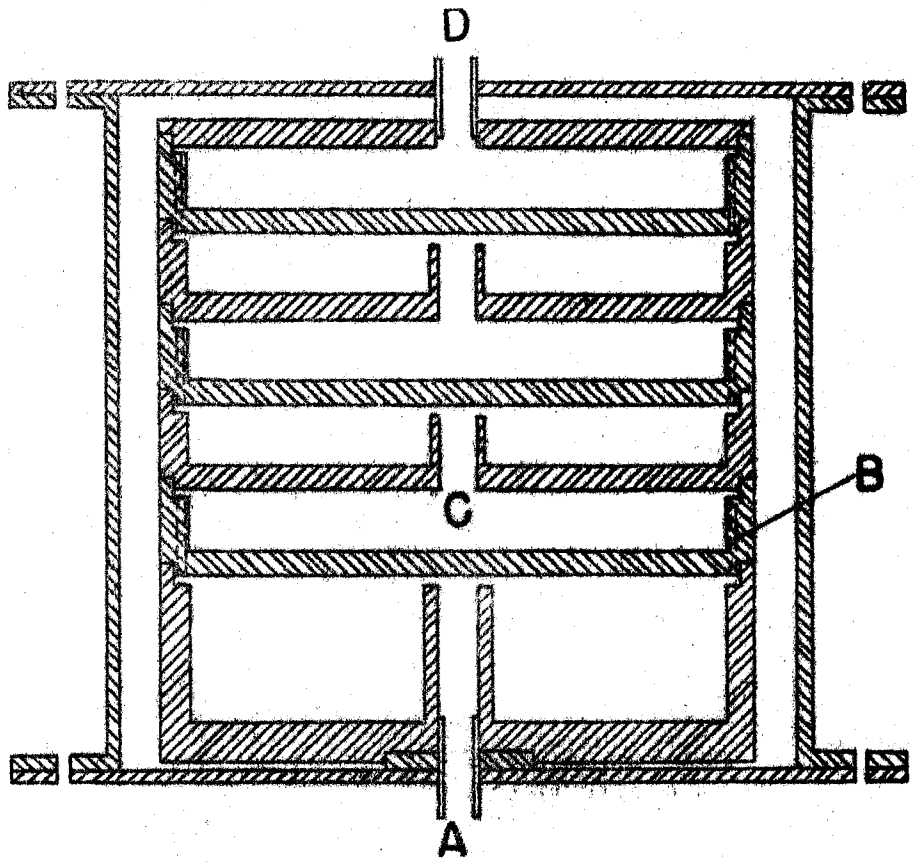
Among the intermediate compounds which could be used for the preparation of zirconium fluoride are zirconium oxide, zirconium tetrachloride, zirconyl chloride, hydrated zirconia, and zirconium carbonate. Zirconyl chloride and zirconium oxide were obtained from the purification process. Hydrated zirconia and zirconium carbonate were formed by precipitation from aqueous solutions of purified zirconyl chloride. Sodium hydroxide and sodium carbonate were employed for this preparation. The precipitations were made in Pyrex beakers and the solutions were vacuum filtered on Buechner funnels. The moist precipitates were dried in stainless steel trays with a current of preheated air.

Zirconium tetrafluoride was made by the low temperature reaction between anhydrous hydrogen fluoride gas and zirconium tetrachloride. This gave an impure zirconium tetrafluoride for use in the preliminary evaluation of the fluoride in the reduction process. Through the use of a vertical assembly of graphite trays enclosed in a copper jacket, the introduction of impurities by corrosion of the container was minimized. Hydrogen fluoride from Pennsylvania Salt

Company was introduced through the bottom (A) of the unit shown in Figure 1. The gas was distributed radially over the charge in the bottom tray. The hydrogen fluoride then ascended through the small ports (B) located on the circumference of the second tray. After passing over the charge of the second tray the gases proceeded to the third tray through the central hole (C). Repetition of this arrangement through any number of trays is possible. The exhaust gases were removed through the copper tube (D) and discharged. A unit consisting of eight trays of 12 inch diameter with a bed depth of two inches had a capacity of 12 kilograms of zirconium tetrachloride per batch. The assembly was jacketed for heating with hot water to prevent condensation of the hydrogen fluoride in the porous graphite.

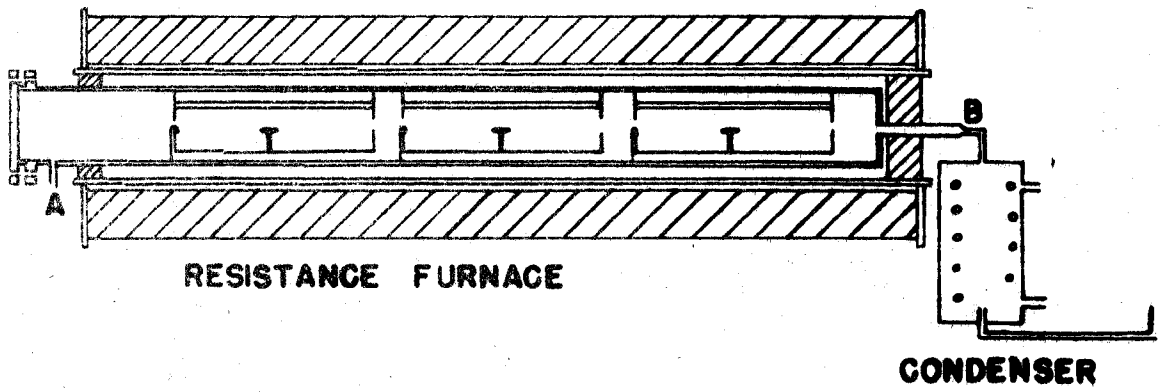
A smaller unit of proportionate size was used for the experimental determination of the conditions for the reaction between zirconium tetrachloride and hydrogen fluoride. This reactor consisted of six graphite trays six inches in diameter. The depth of the charge in each tray was approximately two inches.

The reaction between zirconium oxide or hydrated zirconia with anhydrous hydrogen fluoride proceeded at higher temperatures. The hydrofluorination unit was constructed from Monel metal pipe as illustrated in Figure 2. Hydrogen fluoride from the tank was transported through copper tubing and entered the system through the 1/2 inch Monel tube (A). The gases were directed over the charge in the three trays (T) by semi-circular pieces at the ends of the trays. The exit gases left the system through a 1 inch Monel tube (B).



GRAPHITE TRAY HYDROFLUORINATION UNIT

FIGURE 1



MONEL METAL HYDROFLUORINATION UNIT

FIGURE 2

Disposal of the excess hydrogen fluoride was accomplished by leading the exit gases through 12 feet of 1/2 inch copper tubing enclosed in a water-cooled condenser. The acidic condensate was collected in a Monel bucket and neutralized with sodium carbonate.

The Monel trays were four inches wide and fifteen inches long. The bed of material was approximately one inch deep. The Monel reactor unit was made of six inch pipe 65 inches long. The amount of zirconium fluoride produced in each batch was a function of the bulk density of the starting material, but the average batch gave about five kilograms of product.

Zirconyl chloride or zirconium oxide which contains relatively large amounts of chlorine react with hydrogen fluoride to form hydrogen chloride and water vapor. These reaction products in combination with the excess hydrogen fluoride form a highly corrosive mixture. Monel metal did not adequately withstand this corrosive attack. Trays of other materials, such as copper, silver, and platinum-lined trays were used in the Monel unit. The inner walls of the Monel cylinder were lined with copper sheet.

The Monel hydrofluorination unit was inserted in an iron pipe on which the resistance heating element was located. The design of the resistance furnace gave an unintentional temperature gradient along the length of the tube. The exit end of the Monel tube was usually 80 centigrade degrees hotter than the opposite end and 40 centigrade degrees warmer than the measured temperatures.

The addition of aqueous hydrogen fluoride to solid zirconyl

chloride was tested in reaction vessels made of silver, copper, lead, magnesium, fluorothene, platinum and Bakelite. The reaction mixture was extremely corrosive. The reaction was finally carried out in fluorothene beakers. After decanting the supernatant liquid, the precipitate was transferred to platinum-lined copper trays in which it was dried on a hotplate.

The incomplete conversion of zirconium oxide or hydroxide to the fluoride leaves quantities of oxide which could cause embrittlement of the zirconium produced in the reduction process. Separation of fluoride from oxide was obtained by sublimating the zirconium fluoride in a stainless steel retort on an air-cooled condenser. The retort was heated in a gas-fired furnace. The sublimation operation in an evacuated system gave additional separation from non-volatile or less volatile impurities in the crude fluoride. Abate (19) reported an improvement in the purity of the sublimed zirconium tetrafluoride with the use of a Monel metal liner in the retort and on the condenser.

The experimental reductions of zirconium compounds to the metal were made in a steel bomb as shown in Figure 3. The bomb was constructed of 2.5 inch steel pipe with a welded bottom. The top was threaded and a pipe cap was used for closure. A refractory liner was inserted to prevent interaction of the fused reaction mass with the bomb walls. These liners were either the presintered type or jolt-packed liners formed by jolting the refractory powder around a mandrel. Refractory materials used for the liner were generally electrically fused dolomitic oxide or calcium oxide. Magnorite was used between

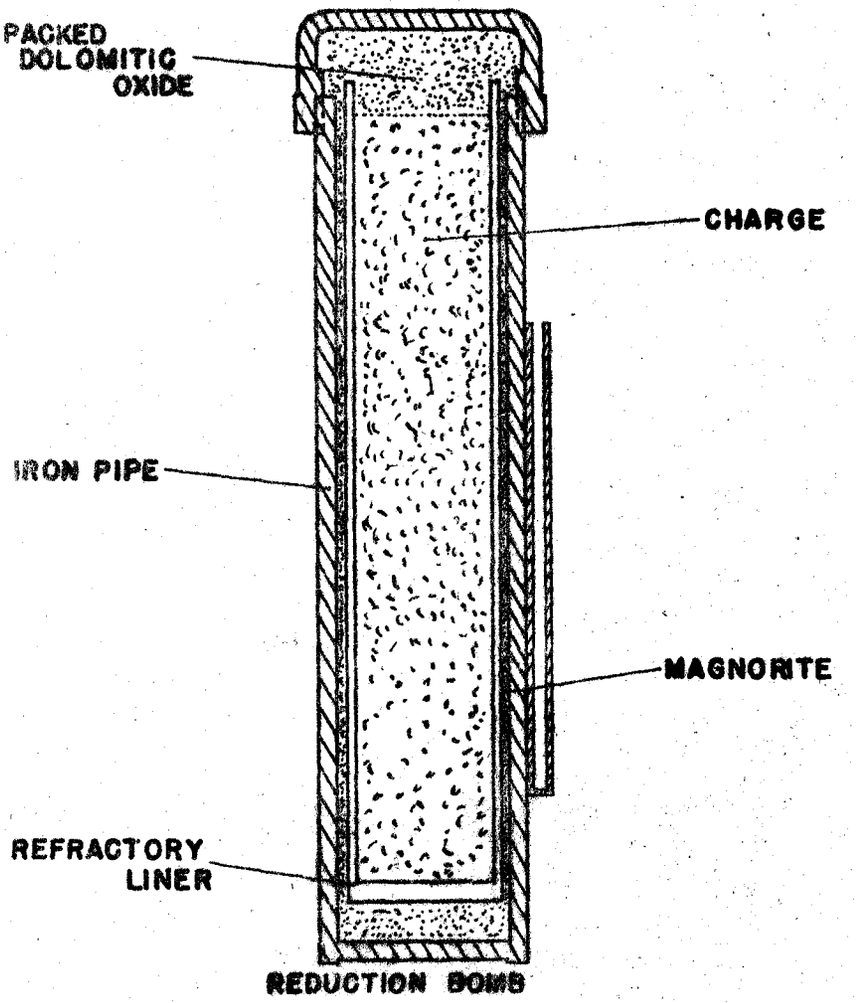

PACKED
DOLOMITIC
OXIDE
CHARGE
IRON PIPE
MAGNORITE
REFRACTORY
LINER
REDUCTION BOMB

FIGURE 3

the presintered liner and the bomb wall to support the liner at the time of firing.

Calcium metal produced at the Ames Laboratory was used as the reducing agent in the reduction of zirconium compounds to the metal. This calcium was redistilled and was of the highest purity available. A typical analysis of the calcium used is reported in Table III to show the amount of contamination which may be introduced in the zirconium metal through the reducing agent.

Table III

Analysis of Calcium Metal

Element	p.p.m.	Element	p.p.m.
Fe	15	Al	7
N	30	Na	<50
Mn	15	Li	<20
C	200	K	<50
Mg	450		

The reaction between the zirconium compounds employed and calcium metal is not initiated at the usual furnace temperatures employed. Thermal boosters were employed which would react with calcium at the furnace temperature and increase the temperature to a point at which the main reaction could proceed. The extremely high melting point of

zirconium favors the addition of an alloying agent to equalize the melting points of the slag and metallic phases of the product. Zinc was found to be a satisfactory alloying agent with the zirconium.

The presence of zinc as part of the booster charge was attained by using zinc chloride or zinc fluoride in the booster reaction. Reagent grade zinc chloride was vacuum dried before it was added to the charge. Zinc fluoride was prepared by the action of hydrogen fluoride on reagent grade zinc oxide at 500 degrees centigrade in the Monel hydrofluorination unit. The hygroscopic nature of zinc chloride and the relative low purity of these materials were disadvantages with the zinc compounds. Bunker Hill zinc metal of extremely high purity was obtained for use as an alloying agent to lower the melting point of zirconium. In this modification resublimed sulfur or iodine was used as the booster reagent.

After loading the charge in the bomb the capped bomb was fired in a gas-fired furnace. This furnace was lined with a 12 inch diameter stainless steel shell and was heated with a ring burner. The furnace temperature was controlled by a Wheelco potentiotrol. The time at which the reaction occurred was detected by measuring the temperature with a thermocouple inserted in a well welded to the side of the bomb. The normal increase in temperature was 25-50 centigrade degrees per minute, but this increased to 100-300 centigrade degrees per minute for the first two minutes after the reaction had taken place. The heating cycle was recorded with a Brown potentiometric recorder.

V. EXPERIMENTAL METHODS

A. Purification of Zirconyl Chloride

The purity attained in the metallic zirconium is partially dependent upon the purity of the zirconium compound employed. In order to achieve the desired purity it was necessary that a purification step should be included. This process had to be applicable to the hafnium-free material from the silica gel columns. It must apply equally to the purification of commercial zirconium tetrachloride for the preparation of a large quantity of material with which to develop subsequent unit processes.

Initial attempts to purify the alcoholic solution of zirconium tetrachloride by ion-exchange methods were unsatisfactory, because the acidity of the solution was too great. Distillation of the methyl alcohol from the solution also removed much of the hydrochloric acid. This operation permitted recycling of the alcohol in the hafnium separation. Aqueous solutions of the solid residue from the methanol recovery were treated by ion-exchange methods with the acid form of Dowex 50 or Nalcite High Capacity resins. The removal of titanium was particularly incomplete and the separation from iron was not too effective.

The composition of the solid remaining after evaporation of the methyl alcohol favored a purification through the crystallization of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$. The residue contained a ratio of one chlorine atom per zirconium atom. The formation of zirconyl chloride

required the addition of hydrochloric acid to meet the stoichiometric requirements and to form a mother liquor of the desired acidity. The hafnium-free material retained most of the impurities present in the original zirconium tetrachloride. A similar treatment of aqueous solutions of zirconium tetrachloride furnished zirconyl chloride free of all impurities except hafnium for use in the development of subsequent processes.

For the preparation of zirconyl chloride of high purity, one kilogram of zirconium tetrachloride was dissolved slowly in water to give four liters of solution. The warm solution was filtered to remove the traces of water insoluble material. Evaporation of the solution adjusted the acidity of the solution to approximately six normal hydrochloric acid. When the solution reached a volume of about 2500 ml., it was cooled with stirring. The cooled solution with the crystalline deposit of zirconyl chloride was vacuum filtered on a Buechner funnel. The crystals were washed with three 500 ml. portions of acetone. Further concentration of the aqueous filtrate to increase the yield of zirconyl chloride was performed in the same manner, but the washing of the crystals became more difficult because of the tenfold increase in the concentration of impurities.

In an expanded scale of this procedure fifteen kilograms of zirconium tetrachloride were dissolved in water to form thirty liters of solution. These quantities gave a solution with the desired acidity without evaporation. The solution was prepared in the glass-lined evaporator in which it could be heated to dissolve all soluble matter.

The deposition of zirconyl chloride occurred throughout the four hour interval required to cool the solution to room temperature. Frequent stirring of the cooling solution prevented adherence of the depositing crystals on the walls of the vessel and was essential for the formation of a crystalline solid with desirable filtration characteristics. Vacuum filtration of the cooled solution retained about 2.5 kilograms of zirconyl chloride on the size 6 Buechner funnel. The filtration of the entire batch gave twenty liters of filtrate, in which the solubility of zirconyl chloride is equivalent to about 36 grams of zirconium oxide per liter. The zirconyl chloride crystals were removed and mixed thoroughly with acetone in an evaporating dish for the first washing. The washing of the crystals was continued on the funnel until the solids gave only a faint test for iron with thiocyanate ion. The water insoluble material in the original zirconium tetrachloride remained with the zirconyl chloride. Prior to its use in subsequent steps, this zirconyl chloride was dissolved in water and filtered. The greater solubility of zirconyl chloride in water as compared with acidic media reduced the volume of solution to be filtered.

The preparation of hafnium-free zirconyl chloride from an aqueous solution of the solid remaining after the recovery of the methyl alcohol followed a similar procedure. Allowances were made to increase the atomic ratio of chlorine to zirconium and for the water of hydration associated with zirconyl chloride in the formation of the acidic solution. The treatment of a batch containing five kilograms of zirconium would require the addition of 12.5 liters of water and 13.5 liters of

concentrated hydrochloric acid.

In most cases the zirconium content of the material received for purification was not accurately known. The residues were dissolved in 1:1 hydrochloric acid and evaporated until a scum of zirconyl chloride appeared. After estimating the volume of the saturated solution, one liter of 1:1 hydrochloric acid was added for mother liquor for each liter of the saturated solution of zirconyl chloride. The solids were dissolved by heating the solution and the crystallization proceeded during the cooling cycle as before. The zirconyl chloride crystals were washed with acetone. More economical use of the acetone was possible by batch recycling. The initial wash was made with acetone from the final washing of the previous batch. For the second wash acetone which had been recovered by distillation was employed. A final wash with pure acetone gave a white product of high purity.

The removal of organic material from the zirconyl chloride was particularly difficult. Carbonaceous material originated during the distillation of methyl alcohol from the hafnium-free solution. This material was soluble in acetone but did not dissolve completely in hydrochloric acid. Zirconyl chloride washed with acetone interacted with residual acetone to form non-volatile organic materials. Removal of material which might contribute carbon as an impurity in the final metal was attempted with the purified zirconyl chloride washed with acetone. The zirconyl chloride was redissolved in water and filtered to remove insoluble matter. The recrystallization of zirconyl chloride was obtained by adding concentrated hydrochloric acid.

The procedure was the same as that used in the original crystallization. After filtering the recrystallized zirconyl chloride, it was washed with 1:1 hydrochloric acid previously saturated with zirconyl chloride. The filtrate and washings were combined and used as the solvent for the hafnium-free solids in a succeeding batch.

B. Ignition of Zirconyl Chloride

The conversion of zirconyl chloride to zirconium oxide was accomplished by ignition at elevated temperatures. The solid zirconyl chloride was charged in closed-end quartz tubes, which were suspended vertically in a gas-fired furnace heated to 600 degrees centigrade. After twenty-four hours a dense white product was obtained which retained only small amounts of carbon and chlorine. The carbon resulted from thermal decomposition of acetone and other materials in the zirconyl chloride. Further ignition at 800 degrees centigrade in a smaller furnace reduced the amount of carbon and chlorine in the zirconium oxide.

The ignition of zirconyl chloride liberated large amounts of water vapor and hydrogen chloride. The condensation of these vapors was accomplished by drawing them through a water-cooled condenser by means of a water aspirator. The condensate was colored by organic matter, but distillation should give aqueous hydrochloric acid which could be used for the purification of zirconyl chloride. No effort was directed toward this economy measure during the preparation of zirconium oxide.

C. Preparation of Zirconium Tetrafluoride

Since zirconyl chloride represented the purified state in the zirconium program, it was necessary to prepare a compound suitable for the reduction process from pure zirconyl chloride. It was assumed that zirconium oxide could be converted to zirconium tetrachloride, if necessary, through the carbide intermediate. Preliminary investigations demonstrated that the double fluorides could be prepared by the use of aqueous potassium, sodium or ammonium fluoride with solid zirconium tetrafluoride or aqueous zirconyl chloride. These materials were available commerciably for the experimental phases of the reduction process.

Zirconium tetrafluoride for study of the reactions capable of producing zirconium metal was not available. It is possible to make zirconium fluoride by treating solid intermediate compounds or solutions with hydrogen fluoride, gaseous or aqueous, or with solutions of soluble fluorides. Zirconium salts react with aqueous solutions of alkali fluorides to give the double fluorides or fluozirconates. Formation of ammonium fluozirconate in this way can be used in the preparation of zirconium tetrafluoride by subsequent heating in vacuum to volatilize the ammonium fluoride as the compound dissociates. The undesirable role of nitrogen in the corrosion resistance of zirconium minimizes the importance of this method.

Material for the initial research on the reduction of zirconium fluoride was prepared by the action of gaseous hydrogen fluoride with zirconium tetrachloride. Although the zirconium fluoride was not pure,

determination of the optimum conditions for the reduction gave the preliminary information for evaluation of zirconium tetrafluoride as a starting material.

Zirconium tetrachloride powder was placed in the graphite trays of the smaller unit similar to that shown in Figure 1. The trays were enclosed in the copper jacket and the unit was attached to the hydrogen fluoride line. The reaction time was studied as a function of the temperature.

The preparation of zirconium tetrafluoride from the chloride is represented by the equation:

$$ZrCl_4 + 4\ HF \longrightarrow ZrF_4 + 4\ HCl$$

The progress of the reaction was followed by an analysis of the exit gases for chloride content. Since the exit gases included excess hydrogen fluoride, it was necessary to modify the Volhard determination of chloride to obtain a rapid analysis for the products of the reaction. Since fluoride ion complexes the ferric ion indicator used in the Volhard method, it was necessary to add aluminum nitrate which exerted a stronger complexing action for fluoride ion than did ferric ions. The usual procedure for chloride was then employed on the sample obtained by dissolving the exit gases in water.

Accurate control of the rate of flow of hydrogen fluoride was not possible with the equipment used. Analysis of the exit gases for total acidity gave the amount of hydrogen fluoride entering the system, since an equivalent of hydrogen chloride is evolved by hydrogen fluoride consumed in the reaction. Comparison of the degree of conversion to

zirconium fluoride for a given input of hydrogen fluoride was made at several temperatures.

Zirconium tetrafluoride made by the low temperature hydrofluorination of zirconium chloride is a powder with about the same bulk density as the chloride. It exhibits the same tendency as zirconium tetrachloride to hydrolyze with atmospheric moisture. Hydrolysis was eliminated by heating the low temperature fluoride at a temperature above 300 degrees centigrade for two hours in an atmosphere of hydrogen fluoride. The Monel metal unit shown in Figure 2 was used for this final treatment. This operation completed the conversion of unreacted zirconium chloride and zirconium oxide formed by hydrolysis during transfer of the tetrachloride and the low temperature fluoride.

Among the methods considered for the preparation of zirconium fluoride were the direct hydrofluorination of zirconyl chloride, treatment of a lower hydrate or a mixture of oxide and oxychlorides with lower water content with hydrogen fluoride, and the preparation of zirconium hydroxide or carbonate as intermediate compounds prior to the hydrofluorination. Gaseous or liquid anhydrous hydrogen fluoride and aqueous hydrofluoric acid were least likely to introduce impurities in the fluoride product.

The combination of water, hydrogen chloride, and hydrogen fluoride formed during the treatment of zirconium compounds containing chloride presented a serious corrosion problem in the choice of materials of construction. The resistance of copper and copper alloys to hydrogen chloride is diminished in the presence of water vapor.

In the reaction between zirconyl chloride and gaseous hydrogen fluoride, a solution of the charge resulted from the combination of the water of hydration with the hydrogen fluoride. The highly corrosive properties of these solutions containing hydrochloric acid and hydrofluoric acid made it desirable to remove the water of hydration from zirconyl chloride prior to the reaction with hydrogen fluoride. Since the displacement of chlorine by fluorine proceeds more readily than the displacement of oxygen in the hydrofluorination reaction, the removal of the water of hydration should be accomplished with a minimum loss of chloride by hydrolysis to zirconium oxide. Zirconyl chloride was heated in the quartz tubes at various temperatures for twenty-four hours to give a material for conversion to zirconium fluoride. Removal of the water of hydration by heating small samples in vacuum and at atmospheric pressure was studied for a method to give a starting material for hydrofluorination.

The oxide with a variable chlorine and water content was crushed with a jaw crusher having an opening of 1/4 inch. The crushed material was placed in the trays and treated with hydrogen fluoride in the Monel metal unit shown in Figure 2. The degree of conversion to zirconium tetrafluoride was determined as a function of the time of hydrofluorination, temperature of the zirconyl chloride ignition, and the temperature of the Monel unit. The amount of corrosion of the trays was a necessary compromise between the time required for conversion to fluoride and the temperature to which the zirconyl chloride was heated before hydrofluorination. Trays of copper, brass, lead, silver, nickel, and platinum

were tested for use as materials of construction for the trays and hydrofluorination unit. Since zirconium tetrafluoride obtained by the treatment of zirconium oxide with hydrogen fluoride retained zirconium oxide and added other impurities as a result of corrosion of the trays, it was purified by sublimation before it could be used in the experimental reduction to metal.

The reaction between zirconium hydroxide and hydrogen fluoride does not evolve gases of a corrosive nature, so the Monel metal unit may be used without contamination of the zirconium fluoride. The removal of chloride ion in the hydroxide by thorough washing of the precipitate is necessary to eliminate the corrosion problem. To a solution containing 400 grams of sodium hydroxide in 12 liters of water was added a solution containing 1610 grams of zirconyl chloride in 8 liters of water. The filtration characteristics of the precipitate was improved by this mode of addition of the reacting solutions. The principal problem in the hydroxide precipitation was the removal of filtrate from the solids. The occluded liquids amounted to 80 per cent of the weight of the wet filter cake. The large volume of the wet cake discouraged direct washing of the hydrous oxide on the Buechner funnel. The cake was dried in stainless steel trays with preheated air which heated the material to approximately 60 degrees centigrade. The dry solids were pulverized and washed, but the removal of sodium chloride was very difficult. The washed zirconium hydroxide was dried in the same manner as the original precipitate. The dry solids were treated with gaseous hydrogen fluoride in the

Monel metal unit for the conversion to zirconium tetrafluoride. Sublimation to eliminate zirconium oxide was employed to give a pure product.

The direct preparation of zirconium fluoride from zirconyl chloride was obtained with the use of aqueous hydrogen fluoride. The addition of 48 per cent hydrofluoric acid to solid zirconyl chloride was made in fluorothene beakers, which satisfactorily resisted the corrosive mixture of acids. The stoichiometric quantity of hydrogen fluoride giving four fluorine atoms per zirconium atom was added to 300 grams of zirconyl chloride in each batch. Stirring the mixture gave a clear solution but the reaction proceeded almost immediately to deposit an hydrated zirconium tetrafluoride product. In the treatment of larger batches complete solution of the zirconyl chloride could not be accomplished before the precipitation reaction occurred. Decantation of the supernatant liquid after the solution had cooled removed 70 per cent of the filtrate, which retained less than two per cent of the original zirconium. Removal of the supernatant liquid gave an additional purification for those materials which form soluble chlorides or fluorides. The wet precipitate of zirconium tetrafluoride was dried in platinum-lined copper trays at 110 degrees centigrade. The dried product was mainly the monohydrate of zirconium tetrafluoride, although hydrolysis during the drying caused minor variations from this composition. Dehydration of the precipitated fluoride was completed in the Monel metal unit illustrated in Figure 2. The Monel metal trays were lined with magnesium to minimize the addition of

undesirable impurities. Magnesium contamination of the crude metal from the reduction would be volatilized in the remelting of the zirconium. The dehydration of 3500 grams of zirconium tetrafluoride monohydrate was completed by heating for five hours in an atmosphere of hydrogen fluoride at 500 degrees centigrade.

D. Reduction of Zirconium Compounds

The reduction of zirconium compounds to the metal was performed in steel bombs lined with a refractory material. The refractory liner was a sintered crucible made from electrically fused dolomitic oxide in most of the experimental reductions. The space between the sintered liner and the walls of the bomb was filled with magnorite to prevent mechanical failure of the liner at the time of reaction. After locating the charge in the liner the top was packed with a layer of dolomitic oxide powder. The pipe cap was filled with a packing of dolomitic oxide powder about one inch thick. After applying a coating of pipe joint cement to the threads of the bomb, the cap was screwed on the bomb to give a tight seal. This assembly, as illustrated in Figure 3, was used in testing materials for the reduction and in the determination of the optimum conditions giving a maximum yield of zirconium metal.

The reaction mixture consisted of the zirconium compound, a booster reagent, and calcium metal. An alloying addition of zinc metal was made, when a zinc compound was not used as the booster reagent. The charge was generally mixed thoroughly and added to

the liner by jolting or by tamping with a wooden dowel.

After loading and capping the bomb, it was placed in the pit of a small gas-fired furnace. By means of a thermocouple located in the well on the side of the bomb, the heating cycle was recorded on a Brown potentiometric recorder. At the time the charge reacted, a sharp increase in temperature resulted from the exothermic heat of reaction. About three minutes after the reaction occurred, the temperature would decrease as the bomb cooled. The bomb was removed from the furnace and allowed to air cool to room temperature.

The choice of the zirconium compound to be used in the reduction process was made after developing a method with potassium fluozirconate. Zinc chloride was used as the booster reagent to supplement the total heat evolved by the reaction and to lower the melting point of the metallic phase of the reaction products. Potassium fluozirconate was combined with a variable amount of zinc chloride and the stoichiometric amount of calcium metal. The charge containing 431 grams of K_2ZrF_6, 71 grams of zinc chloride, and 143 grams of calcium metal gave the best yield in the 2.5 inch bomb with a sintered dolomitic oxide liner.

Substitution of zirconium tetrachloride for the potassium fluozirconate increased the exothermic heat of reaction. A decrease in the amount of zinc chloride was possible without detracting from the yield of zirconium metal. The formation of an alloy containing 12 per cent zinc by weight gave the maximum yield of zirconium metal in the reduction of zirconium tetrachloride.

Since some calcium metal is trapped by the slag, part of it

becomes alloyed with the zirconium, and small amounts are used in the formation of sub-halides, the use of excess calcium was investigated. An increase in the yield of zirconium metal was obtained with the addition of excess calcium. A charge containing 300 grams of zirconium tetrachloride, 45 grams of zinc chloride, and 128 grams of calcium proved most satisfactory. This included a ten per cent excess of calcium.

Using the same molar proportions in the charge, replacement of zirconium tetrachloride by zirconium tetrafluoride made by hydrofluorination of zirconium tetrachloride improved the yield of zirconium metal so markedly that all further investigations were made with the fluoride as starting material. Since zirconium tetrafluoride can be treated so it does not hydrolyze in air, this factor in the preparation of the charge was important.

After the experimental conditions which gave the maximum yield of zirconium metal were determined, attention was directed to an improvement in the physical properties of the metal. The extreme brittleness of the metal could probably be attributed to oxygen, possibly introduced from the following sources:

1. Zirconium oxide content of the zirconium tetrafluoride.
2. Calcium oxide formed by the action of calcium metal with air during storage.
3. Water added with the hygroscopic zinc chloride during preparation of the charge.
4. Residual air in the bomb after adding the charge.
5. Interaction of the reaction products with the liner.

The separation of zirconium oxide from zirconium tetrafluoride was attained by a vacuum sublimation of the fluoride at 750 to 800 degrees centigrade. A stainless steel retort containing the crude fluoride was heated in a gas furnace. The sublimed fluoride was condensed on a cylinder cooled by air. The product was a dense crystalline material which was difficult to grind. Some contamination with iron occurred, but the substitution of a container of Monel metal and a Monel condenser inserted in the stainless steel retort overcame this difficulty. Some purification of the crude fluoride from other metallic impurities has been obtained by Abate (19).

The introduction of oxygen with the reducing agent was minimized by using the calcium shortly after it was prepared by distillation. The calcium was packed in small sealed containers in an argon atmosphere to avoid exposure to the atmosphere.

Oxygen introduced as water with the zinc chloride could be eliminated only by the use of specialized methods in the preparation of the charge. Such specialized methods are not readily applicable in an expanded routine production process. The use of zinc fluoride, prepared by treating zinc oxide with hydrogen fluoride at 500 degrees centigrade, was not successful. This was probably the result of incomplete conversion of zinc oxide to zinc fluoride.

The use of zinc turnings with sulfur or iodine as the booster reagent gave the lower melting alloy of zinc and zirconium. This combination avoided the use of oxygen-containing materials and hygroscopic reagents. With sulfur or iodine to supply the desired

thermal effect it became possible to form alloys of lower zinc content. The addition of these materials introduced new variables which might affect the yield of the zirconium product. Increasing the iodine or sulfur made it possible to produce a crude zirconium metal in the massive form, without an alloying addition of zinc metal. However, the high temperatures required increased the amount of attack of the refractory liner by the product.

After packing the liner in the bomb this part of the assembly was flushed with argon for five minutes to reduce the effect of residual air. An improvement in this technique was obtained by evacuating the bomb and liner and filling with argon three times. The mixing bottle containing the reaction charge was flushed with argon to displace the air. With reaction charges containing an iodine booster the evolution of iodine vapors while loading the bomb aided in the removal of air.

Control of the effects of the attack on the refractory liner by the charge or the reaction products could be approached in two ways. Decreasing the maximum temperature reached in the bomb or the use of more refractory materials than dolomitic oxide could improve the quality of the zirconium metal. The maximum temperatures obtained in the bomb could be diminished by the use of smaller amounts of the booster reagent. The addition of a chemically inert material to serve as a fluxing agent would also consume part of the evolved heat during the fusion of the products.

Substitution for the dolomitic oxide liner was tested with calcium oxide, magnesium oxide, or calcium fluoride liners and by lining the

dolomitic oxide refractory with calcium fluoride, tantalum or molybdenum sheet. The reduction charge remained constant with 400 grams of zirconium tetrafluoride, 40 grams of zinc metal, 216 grams of iodine, and 248 grams of calcium metal. The alloy of zirconium and zinc was heated in vacuum to volatilize the zinc, then cast in graphite. The hardness of the cast metal served as an indication of the amount of oxygen introduced by interaction with the refractory.

After the testing of the refractory liners had reduced the list of potential materials to calcium oxide and dolomitic oxide, the effect of a decrease in the amount of iodine in the charge was determined. Initially the iodine was decreased to determine the change in yield of zirconium metal which might result. When it was found that decreasing the amount of iodine in the charge to 64 grams did not change the yield of zirconium, a charge containing 400 grams of zirconium tetrafluoride, 40 grams of zinc metal, 64 grams of iodine, and 223 grams of calcium metal was used. Sintered refractory liners of calcium oxide and dolomitic oxide were tested with the above charge. Variations were made in the method of removing the zinc and casting the zirconium metal for a final evaluation of the refractory materials.

E. Analytical Methods

Chemical analyses of zirconium and its compounds were necessary to assure the completeness of the purification of zirconyl chloride, to ascertain the degree of conversion to the compound to be reduced, and to make certain that impurities were not introduced in the reduction

step in amounts which might impair the corrosion resistance or the physical properties of the metal. Spectrographic analyses were obtained for some of the elements which could not be determined by chemical methods and to verify the results obtained from chemical data.

The methods for the determination of titanium, iron, manganese, nitrogen, nickel, and zinc were developed by A. S. Ayres (20). The analyses were made with aliquots of the zirconium sample in sulfuric acid. Zirconyl chloride was dissolved and heated with sulfuric acid. Copious fuming of sulfur trioxide was continued until the chloride ions were removed. The treatment of zirconium tetrafluoride by heating with sulfuric acid in a platinum dish completed the dissolution of the sample. Repeated evaporations to dryness removed fluoride ions. Samples of zirconium oxide or zirconium metal were placed in a large platinum dish and covered with dilute sulfuric acid. Hydrofluoric acid was added dropwise to dissolve the sample. The solution was heated to copious fumes of sulfur trioxide for half an hour to remove fluoride ions. The cooled solutions of the zirconium samples were transferred to volumetric flasks from which aliquots were removed for the analysis for the individual elements. Each sample contained approximately 10 grams of zirconium.

The colorimetric determination of titanium involved the formation of the yellow pertitanate ion by the addition of hydrogen peroxide to an aliquot of the zirconium sample in sulfuric acid. Using a sample containing one gram of zirconium, titanium in zirconium can be determined as low as 10 parts per million. The color was developed rapidly

by the addition of hydrogen peroxide. The solution was transferred to a five centimeter cuvette and the transmittancy measured against water as a reference at 410 mμ in the Coleman spectrophotometer. Comparison with a previously prepared standard curve gave the titanium content of the solution.

An aliquot containing one gram of zirconium, with which values as low as 5-10 parts per million of iron in zirconium can be determined, was treated with hydroxylamine hydrochloride to reduce the iron to ferrous iron. The addition of 1,10-phenanthroline caused the formation of the red ferrous sulfate-1,10-phenanthroline complex. The maximum color was developed at a pH of 5-7, which required the addition of ammonium tartrate to prevent the precipitation of zirconium. After a one hour interval to allow the color to develop, a portion of the solution was transferred to one centimeter cuvettes. The per cent transmission of the solution was determined in the Coleman spectrophotometer at 515 mμ with water as a reference. With the value found in this manner the iron content of the solution was determined from a previously prepared standard curve.

Manganese was determined colorimetrically by the development of the purple permanganate color which was formed by treating the solution of zirconium with silver nitrate and ammonium persulfate. The transmittancy of the purple solution was measured in the Coleman spectrophotometer using water as a reference solution at a wave length of 545 mμ. Comparison with the standard curve gave the manganese content of the solution.

Nitrogen was determined by the Kjeldahl method. Following the addition of tartaric acid and sodium hydroxide to an aliquot of the zirconium solution, steam was passed through the mixed solution until 50 ml. of the distillate had been collected in a solution of boric acid and methyl purple indicator which had been added to the vapor trap and receiver of the apparatus. The distillate was titrated with standard hydrochloric acid to a neutral gray end point. The necessary corrections for the indicator and reagent blank were made before calculating the nitrogen content of the solution.

An aliquot removed for the determination of nickel and zinc was adjusted to a final pH of 8.0 after the addition of sulfosalicylic acid. About 10 ml. of this solution was used in a Sargent Model XII polarograph. Nickel appears at a half-wave potential of -0.95 volts and zinc is observed at -1.20 volts as measured against the saturated calomel cell. The instrument was calibrated by the standard addition method. Volumes of a standard zinc solution and a standard nickel solution containing approximately the same amounts as that found in the zirconium sample were added to another aliquot of the solution of the sample. The mixture was given the same treatment as the original sample.

The determination of carbon in zirconium tetrafluoride was made with a usual carbon train modified by having a scrubbing tower filled with a saturated solution of aluminum sulfate in 1:1 sulfuric acid to remove hydrogen fluoride. A glass wool plug was also inserted to filter the dust from the fluoride. An ignition at 1800 degrees Fahrenheit

for 45 minutes was required for the determination. Carbon in zirconium metal was determined by burning turnings of the metal in an alundum boat. Sulfur was converted to sulfur trioxide with platinized asbestos and activated manganese dioxide on asbestos.

The determination of fluorine in zirconium tetrafluoride was important in showing the purity of the compound to be reduced. The pyrohydrolytic method of Warf and Cline (21) was used to convert zirconium tetrafluoride into zirconium oxide and hydrogen fluoride. Steam was passed over the sample in a platinum boat heated to 800-850 degrees centigrade. The steam and hydrogen fluoride were condensed and collected in a silver dish. A titration of the distillate with standard sodium hydroxide in the presence of phenolphthalein indicator gave the fluorine content of the sample. In the case of sublimed zirconium tetrafluoride the pyrohydrolysis reaction took a long period of time to remove the last traces of fluorine.

Samples prepared for the analysis of other impurities by spectrographic methods were converted to the oxide. Zirconium tetrafluoride severely limited the spectrographic determinations, so fuming with sulfuric acid was necessary to convert the zirconium tetrafluoride to the sulfate, which could be ignited to zirconium oxide. Metal samples were burned in air to form the oxide.

VI. EXPERIMENTAL RESULTS

The development of a process for zirconium metal included the purification of zirconyl chloride, conversion of zirconyl chloride into a compound suitable for the reduction step, and the application of a reduction process capable of giving zirconium of suitable purity. Following the purification of zirconium as zirconyl chloride, the introduction of undesirable impurities during subsequent steps had to be minimized. The reduction to the metal required an evaluation of the various zirconium compounds for use as the starting material. The use of supplementary reactions in the bomb reduction to supply additional heat and the addition of alloying materials to lower the melting point of zirconium were investigated relative to the efficiency of the reduction process and to the purity of the metallic product.

A. Purity Attained in Zirconyl Chloride Purification

The white crystalline solid obtained in the purification by deposition from an acidic medium on cooling retained only small amounts of the original metallic impurities. After air drying the material at room temperature, analysis showed that the purified product corresponded to the formula $ZrOCl_2 \cdot 8H_2O$. Aqueous solutions of the purified zirconyl chloride were colorless and exhibited no turbidity which might interfere with colorimetric analytical procedures. The high degree of purity attained with the zirconyl chloride crystallization was utilized in the development of analytical curves for chemical and spectrographic analyses of zirconium metal and other compounds at the Ames Laboratory

and other installations of the Atomic Energy Commission.

The chemical and spectrographic analytical results are reported in Table IV as parts per million of the impurity in zirconium oxide. The range of values includes the results for several samples. In addition the following elements were not detected: lead, beryllium, manganese, arsenic, chromium, germanium, molybdenum, nickel, antimony, tin, vanadium, zinc, and bismuth.

Table IV

Analysis of Zirconyl Chloride

Element	p.p.m. in ZrO_2	Element	p.p.m. in ZrO_2
Fe	15-50	Al	0-30
Hf	<500	Mg	<5
Ti	10-40	B	0-3
Si	<20	Ag	0.2-0.5

The analysis of zirconyl chloride for carbon could not be performed readily, since an ignition in a carbon train would liberate hydrogen chloride by hydrolysis. The presence of carbonaceous matter was evident from the analysis of zirconium oxide. The reduction of the carbon impurity during the conversion to zirconium tetrafluoride removed the need for developing an analytical method for carbon in zirconyl chloride. The removal of carbon was more serious with the

hafnium-free material because of the methanol decomposition.

B. Production of Zirconium Oxide

Zirconium oxide was prepared to supply a pure hafnium-free material for testing in the iodide decomposition (7) and Bureau of Mines (10) processes for metallic zirconium at other laboratories of the Atomic Energy Commission. Four lots of material giving a total of 100 pounds of zirconium oxide were processed through the zirconyl chloride purification step followed by ignition in quartz tubes. The hafnium content

Table V

Analysis of Zirconium Oxide

Lot No.	Temperature of Ignition, °C.	Carbon p.p.m.	Chlorine, p.p.m.	Iron p.p.m.	Titanium, p.p.m.
1	600	630	3095	48	35
2	800	275	810	47	54
3	600	595	2815	45	27
4	600	675	3200	12	3

had been reduced to less than 500 parts per million by the silica gel adsorption method (4). The analytical results for the major impurities are presented in Table V for each of these lots of zirconium oxide. The values for the other impurities were included in Table IV.

The data shown in Table V demonstrate the feasibility of a purification by crystallization of zirconyl chloride on an engineering scale.

The quantities of carbon in zirconium oxide reveal the presence of organic matter in the zirconyl chloride which had been washed with acetone. Reduction of this carbon content during the zirconyl chloride purification or in subsequent processes was necessary in order to obtain a metallic product sufficiently free from carbon.

The lower values for iron and titanium obtained in Lot 4 were attributed to the use of recovered acetone for washing the zirconyl chloride crystals. This acetone had been recovered by distillation of the washings from preceding batches. It retained small amounts of hydrochloric acid from the displaced mother liquor. The increased efficiency of the purification process led to the inclusion of recovered acetone for part of the washing operation in subsequent production of zirconyl chloride.

C. Preparation of Zirconium Tetrafluoride

Material for the initial investigation of the feasibility of using zirconium tetrafluoride in the reduction charge was obtained by the low temperature treatment of zirconium tetrachloride with hydrogen fluoride. The total acidity of the exit gases measured the rate at which hydrogen fluoride was introduced. The chloride analysis of the exit gases indicated the rate at which hydrogen fluoride was consumed. The degree of conversion was calculated from the cumulative chloride evolved and the total theoretical chloride to be displaced from the zirconium tetrachloride charge. Comparison of the degree of conversion at three different temperatures as a function of the amount of hydrogen fluoride

introduced into the system is made in Table VI.

The degree of conversion to zirconium tetrafluoride based on the chloride content of the exit gases was lower than the value obtained from a fluoride analysis of the product. The sampling of gases from the exit stream probably led to low results because of losses. It is apparent from the data that the lowest temperature gives more rapid conversion to zirconium tetrafluoride by making more efficient use of

Table VI

Conversion of Zirconium Tetrachloride
to Zirconium Tetrafluoride

HF input, grams	% conversion at 50°C.	% conversion at 80°C.	% conversion at 100°C.
100	15.0	10.2	13.6
200	29.1	21.2	25.0
300	42.2	32.6	34.5
400	55.8	43.0	44.9
500	68.4	52.9	55.2
600	78.5	61.2	62.2
700	85.2	68.7	68.7
800	88.2	74.6	72.2

the hydrogen fluoride. The use of still lower temperatures was discouraged by the condensation of hydrogen fluoride in the porous graphite trays.

With the smaller unit of the type shown in Figure 1 a charge of

1500 grams of zirconium tetrachloride was converted to the fluoride in 6.5 to 8 hours. The time depended on the rate of addition of hydrogen fluoride. In the larger unit 12 kilograms of zirconium tetrachloride required 20-24 hours for the completion of the reaction.

Hydrolysis of the low temperature fluoride by atmospheric moisture, which created a problem in the storage of the material and was a serious disadvantage during the preparation of the reduction charge, was effectively eliminated by heating the zirconium fluoride in an atmosphere of hydrogen fluoride above 300 degrees centigrade for two hours. Any oxide or oxyhalide products resulting from the hydrolysis were changed to zirconium tetrafluoride during this treatment. The final product usually contained about 45.0 per cent fluorine and less than 0.1 per cent chlorine. Sublimation of this crude zirconium tetrafluoride volatilized 98.6 per cent of the material. The residue contained iron as the major constituent, so most of the zirconium was present as fluoride. The sublimate contained 45.3 per cent fluorine, which compares very favorably with the theoretical value if allowances are made for impurities.

Sublimation of the crude zirconium tetrafluoride by heating to 800 degrees centigrade in vacuum greatly increased the bulk density of the fluoride. An improvement in the purity of the zirconium tetrafluoride was obtained. Some fractionation from hafnium fluoride occurred, but zirconium tetrafluoride was the more volatile so a separation of zirconium and hafnium by sublimation does not seem practical.

The reaction between zirconium oxide and hydrogen fluoride did not proceed at a favorable rate. The low temperature ignition of zirconyl chloride gave a more reactive material for the preparation of zirconium tetrafluoride. The amount of chloride remaining in the oxide depended on the temperature of the ignition. Ignition of zirconyl chloride at 400 degrees centigrade gave zirconium oxide containing about one per cent chlorine. This oxide did not react readily with hydrogen fluoride in the temperature range of 200 to 500 degrees centigrade. Zirconyl chloride heated to 300 degrees centigrade retained 7.2 per cent chlorine after a 24 hour ignition of a batch giving 10 pounds of product. Zirconium oxide from this ignition required an excessive amount of time for the conversion to zirconium tetrafluoride, although it was an improvement over the oxide prepared at higher temperatures.

As much as 19.7 per cent chlorine remained after heating zirconyl chloride at 250 degrees centigrade for 24 hours. This material reacted readily with hydrogen fluoride. During the early stages of the reaction the hydrofluorination was operated at 200 degrees centigrade. The replacement of chlorine by fluorine occurred completely during the first four hours. Elevation of the temperature to 400 degrees centigrade accelerated the hydrofluorination of the remaining zirconium oxide.

Corrosion of the Monel metal unit and the introduction of impurities in the product were excessive in the hydrofluorination of

material formed by the ignition of zirconyl chloride at temperatures below 250 degrees centigrade. Zirconium fluoride prepared from the oxide ignited at 250 degrees centigrade contained 0.05 to 0.20 per cent nickel. Sublimation of this fluoride did not remove all of the nickel. Zirconium metal obtained from this sublimed fluoride was suitable for the development of dezincing and casting operations by other sections of the Ames Laboratory.

Other materials were tested for use in the construction of trays in the hydrofluorination unit. Lead, brass, silver, nickel and stainless steel trays led to the addition of undesirable impurities in the fluoride product. Copper was an improvement over Monel metal, but zirconium tetrafluoride prepared from zirconium oxide in copper trays contained 0.03 to 0.1 per cent copper. The copper contamination could be reduced to 50 parts per million in zirconium fluoride in the sublimation process. Platinum trays were very effective in limiting the amount of contamination, but the cost for equipment of productive capacity would be too great.

Hydrated zirconia was precipitated from aqueous solutions of zirconyl chloride with carbonate-free sodium hydroxide. Hydrofluorination of hydrated zirconia required 16 hours treatment at 400 degrees centigrade. Zirconium tetrafluoride prepared in this manner contained 500 to 1000 parts per million of carbon, which would be an undesirable addition to the metal product. The conversion to the fluoride was about 95 per cent complete, so a sublimation operation was necessary to remove the oxide.

Zirconium tetrafluoride of high purity was obtained by the addition of aqueous hydrogen fluoride to solid zirconyl chloride. The original precipitated fluoride was dried in air to the monohydrate. Analysis of six batches of 1000 grams of the dried precipitate gave an average value of 40.5 per cent fluorine and 49.0 per cent zirconium, which corresponds nearly to the composition of the monohydrate. Dehydration in an atmosphere of hydrogen fluoride completed the conversion to anhydrous zirconium tetrafluoride. The weight of the dehydrated product averaged 90.3 per cent of the weight of the charge in eight batches. The fluorine content of the anhydrous zirconium tetrafluoride was 45.4 per cent and the zirconium content determined as zirconium oxide was 54.3 per cent. No corrections were made for the hafnium content in the determination of zirconium.

The analytical values reported for the chemical determination of the impurities in precipitated and dehydrated zirconium tetrafluoride confirm the high purity retained during the preparation. The high degree of conversion to the fluoride and the high purity of the product eliminated the need for a purification by sublimation. For zirconium tetrafluoride prepared from zirconyl chloride which had been recrystallized and washed with hydrogen chloride, the analytical values in parts per million in zirconium fluoride were: Fe, 17; Ti, 10; N, 12; Ni, <20; Si, 35; and C, 50. The low carbon content of the anhydrous zirconium tetrafluoride was particularly important, since zirconium fluoride from other methods contained more than 500 parts per million of carbon.

D. Experimental Reduction of Zirconium Compounds

The applicability of the bomb reduction method to the preparation of massive zirconium metal was demonstrated by the reduction of potassium fluozirconate with calcium. The metal was recovered as an alloy with zinc. The zinc addition was obtained with the use of zinc chloride as the thermal booster. Under the most favorable conditions zirconium was recovered in a 60 per cent yield as a zinc alloy containing only 70 per cent zirconium. The distillation of a volatile component through the refractory liner during the reduction made it difficult to remove the reaction products from the bomb. The high zinc content of the alloy would necessitate a lengthy vacuum heating operation to volatilize the zinc.

The substitution of zirconium tetrachloride for potassium fluozirconate in the reduction charge increased the heat of reaction. This permitted a decrease in the quantity of zinc chloride used as the booster reagent. The yield of zirconium metal recovered in the regulus was also increased by the use of excess calcium. The maximum yield of zirconium metal was 71 per cent in an alloy with zinc which contained 88 per cent zirconium. The difficulties encountered in handling zirconium tetrachloride and the freezing of the reaction products in the bomb through sublimation of zirconium tetrachloride were serious disadvantages.

Bomb reductions of zirconium tetrafluoride gave an increase in the yield of zirconium recovered. With the amount of zinc chloride

as the variable in the reduction charge, the maximum yield of 85 per cent was obtained with a charge containing a ratio of 1 mole of zirconium tetrafluoride, 0.25 moles of zinc chloride and 2.475 moles of calcium. This charge included a 10 per cent excess of calcium. In a similar series of reductions with stoichiometric quantities of calcium the regulus contained a maximum of 70 per cent of the zirconium. This confirmed the effect of excess calcium in the charge, which was also observed in the reduction of zirconium tetrachloride.

The use of sublimed zirconium tetrafluoride in the charge which contained zinc chloride and a 10 per cent excess of calcium increased the zirconium yields to 93 to 95 per cent. The metal remained brittle after removing the zinc and casting in graphite crucibles. This suggested that oxide contamination from other sources was responsible for the unfavorable physical properties.

The oxygen content introduced as water with hygroscopic zinc chloride was eliminated by changing to iodine or sulfur as the thermal booster reagent. The effect of residual air in the bomb was reduced by sweeping the bomb and liner with argon. Calcium metal which had been recently distilled was also used. Under these conditions the zirconium metal, after the removal of zinc, was found to be extremely hard, but it could be machined and rolled.

The use of sulfur or iodine as the booster reagent made it possible to form a crude zirconium regulus or "biscuit" in a direct reduction of zirconium tetrafluoride without an alloying addition of zinc. A charge containing 300 grams of zirconium tetrafluoride, 338

grams of iodine, and 225 grams of calcium gave 95-98 per cent yields of an impure zirconium metal. The same results were obtained by replacing the iodine with an equivalent amount of sulfur. After vacuum melting the metal in graphite crucibles, the zirconium products were hard. This hardness probably resulted from the increased attack of the liner which occurred at the high temperatures reached in the bomb.

Through the addition of zinc metal to lower the melting point of the zirconium phase, the quantity of iodine or sulfur required in the reduction was decreased. This decrease in the amount of booster used reduced the maximum temperatures reached in the bomb as a result of the exothermic heat of reaction of the charge. Zinc metal was added to the reduction charge in quantities sufficient to produce alloys with zirconium containing 5 and 15 per cent zinc. An addition of zinc metal designed to furnish a zirconium alloy containing 10 per cent zinc resulted in a sharp decrease in the yield of zirconium.

Alloys of zirconium and zinc prepared by a reduction with a sulfur booster retained some of the sulfur. This was not removed during the vacuum heating and casting operation. The sulfur content of the cast zirconium remained as high as one per cent. The metal was quite ductile and there was no apparent effect on the physical properties of zirconium metal which contained sulfur. Since no information was available on the effect of sulfur on the corrosion properties of zirconium, this phase of the experimental work was terminated in favor of the use of an iodine booster.

In an attempt to reduce the oxide contamination resulting from interaction with the bomb liner, other materials were substituted for the dolomitic oxide refractory. These materials were judged on the basis of the yield of zirconium metal obtained, purity of the product, and the hardness of the dezinced and cast metal product. Calcium fluoride was fused to such an extent that the metallic phase came in contact with the walls of the bomb and alloyed with the iron bomb. Tantalum and molybdenum sheet were used inside the refractory dolomitic oxide liner, but excessive alloying between the metal liner and zirconium occurred. Sintered magnesium oxide liners gave a very brittle cast zirconium product, probably as a result of partial reduction of the magnesium oxide by zirconium. Sintered liners of calcium oxide gave the greatest improvement in the quality of the metallic zirconium.

Zirconium metal of improved physical properties was obtained by decreasing the amount of iodine used in the charge. The yield of zirconium metal was decreased in the reduction of sublimed zirconium tetrafluoride with a lower booster content of the charge. With zirconium tetrafluoride prepared by the precipitation and dehydration process the yield of zirconium metal remained at 95 per cent with a fourfold decrease in the amount of iodine. The reduction charge was finally stabilized for the 2.5 inch bomb at 400 grams of zirconium tetrafluoride, 40 grams of zinc metal, 64 grams of iodine, and 223 grams of calcium. With this charge zirconium metal of satisfactory physical properties was obtained with the use of dolomitic oxide

or calcium oxide liners.

The chemical purity of the zirconium metal was improved with the use of the precipitated and dehydrated zirconium tetrafluoride. Among the impurities which were most difficult to control were carbon, iron and nitrogen. The carbon contamination originated from that present

Table VII

Chemical Purity of Zirconium Metal

Element	p.p.m.	Element	p.p.m.
Al	20-30	Mg	5-15
B	1.2-3.3	Ni	<10
Ca	10-60	Si	30-100
Co	<10	Ti	10-20
Cr	<10	Mn	15-25
Cu	10-50	N	60-175
Fe	150-300	Zn	5-40
C	300-500		

in the reaction charge as impurities in the reacting materials and in the dolomitic oxide liner. The formation of carbonates during the intervals that the dolomitic oxide was exposed to the air was probably responsible for the variations in the carbon content as a result of thermal decomposition of these carbonates at the time of reaction. Iron was probably introduced as a result of the sublimation of iodine

from the reduction charge into the liner or to the bomb walls where volatile iodides of iron were formed. Variations in the quantity of nitrogen present in zirconium metal produced by the bomb method could not be adequately explained.

The range of analytical values reported for zirconium metal is included in Table VII. Purification had been obtained by crystallization of zirconyl chloride, followed by conversion to anhydrous zirconium tetrafluoride by the precipitation and dehydration process. The zirconium tetrafluoride was bomb reduced in a sintered dolomitic oxide liner. The alloy of zirconium and zinc was heated by induction in a vacuum to 1700 degrees centigrade to remove zinc, calcium, magnesium and other volatile impurities.

Silicon contamination was increased to an average value of 500 parts per million in zirconium in the reductions in which the bomb was lined with a sintered calcium oxide refractory liner. Carbon contamination was slightly higher in metal produced with a calcium oxide liner.

The possibilities of expanding the scale of the reduction process were investigated with a bomb made of four inch diameter pipe and fourteen inches in length. The bomb was lined with a jolt-packed liner of dolomitic oxide. The charge contained the same relative proportions of reacting materials as had been used with the smaller bombs. Approximately 700 grams of zirconium metal were recovered in each reduction. The yield was decreased to 90 per cent because the

liquid phases of the fused reaction products soaked into the more porous liner. As the size of the bomb is increased further, this factor would be less important, since the ratio of surface area to volume would be more favorable for increased yields of zirconium.

VII. SUMMARY

Zirconium metal in the massive form was prepared in a sealed bomb through the use of an exothermic chemical reduction capable of producing sufficient heat to fuse the reaction products. The metallic phase, which was immiscible with the slag phase of the molten reaction products, contained an alloying addition of zinc metal to decrease the melting point and to diminish the interaction with the refractory liner inserted in the bomb. Reductions of potassium fluozirconate, zirconium tetrachloride, and zirconium tetrafluoride were made by the bomb method.

Hafnium-free zirconium was freed from other metallic impurities by crystallizing zirconyl chloride from hydrochloric acid solution. Acetone was used to wash the crystals from the first crystallization. The crystals of zirconyl chloride were dissolved, filtered and recrystallized from hydrochloric acid solution. Zirconyl chloride from the second crystallization was washed with dilute (1:1) hydrochloric acid saturated with zirconyl chloride. Contamination of zirconium and zirconium compounds prepared in subsequent processes was reduced with respect to carbon by this recrystallization process.

The addition of 48 per cent hydrofluoric acid to solid zirconyl chloride in fluorothene beakers first formed a solution from which zirconium tetrafluoride monohydrate soon precipitated. The supernatant liquid was decanted and the precipitate was dried in platinum-lined copper trays. Conversion to anhydrous zirconium tetrafluoride

was completed by dehydrating the monohydrate in an atmosphere of hydrogen fluoride. The dehydration was made at 500 degrees centigrade in five hours using magnesium-lined Monel metal trays in a reactor constructed of Monel metal. This fluoride product retained the high purity obtained in the zirconyl chloride crystallization.

Zirconium tetrafluoride was also prepared by the action of hydrogen fluoride gas with zirconium tetrachloride at 50 degrees centigrade in graphite trays enclosed in a copper container. Ignition of zirconyl chloride at 250 degrees centigrade gave a material which could be treated with gaseous hydrogen fluoride to furnish zirconium tetrafluoride. Vacuum sublimation at 750-800 degrees centigrade of zirconium tetrafluoride made by these methods was a necessary purification step to remove oxide and other impurities. The sublimed product was not conveniently obtained as pure as zirconium tetrafluoride from the precipitation and dehydration process.

The zirconium compounds were reduced in a steel bomb lined with a sintered dolomitic oxide crucible. Zirconium tetrafluoride was the most satisfactory starting material in the reduction with calcium. The use of iodine with calcium in the reduction charge initiated the reaction between zirconium tetrafluoride and calcium and supplied additional heat to fuse the reaction products. Sulfur could be used in place of iodine, but complete removal of sulfur from the zirconium product was not possible. An alloying addition of zinc metal in the reduction charge decreased the interaction with the refractory liner, since less iodine or sulfur was necessary to fuse the lower melting

alloy of zirconium and zinc. The recovery of zirconium metal was more efficient with the use of excess calcium. Ductile zirconium metal was obtained with a reduction charge containing 400 grams of zirconium tetrafluoride, 40 grams of zinc, 64 grams of iodine, and 223 grams of calcium.

The refractory liner was placed in the steel bomb and this part of the assembly was evacuated and filled with argon three times. The reduction charge was thoroughly mixed and packed in the liner of the bomb. After the bomb was capped the reaction was initiated by heating the bomb assembly in a gas-fired furnace. The regulus recovered was an alloy of zirconium and zinc containing 93-95 per cent of the zirconium. The zirconium content of the alloy was about 85 per cent by weight, although this could be increased by lowering the quantity of zinc included in the reduction charge. Induction heating of the alloy in vacuum removed zinc, calcium, and other volatile impurities. Although some impurities were introduced with the other components of the reduction charge, zirconium metal of high purity was obtained. The practical use of larger bombs with larger charges was demonstrated.

VIII. LITERATURE CITED

1. Unpublished work, S. Naymark, Argonne National Laboratory.

2. Unpublished work, H. B. Fairchild, Oak Ridge National Laboratory.

3. Boulger, F. W., AECD-2726, Declassified Report, Atomic Energy Comm. (March 1949).

4. Hansen, R. S. and K. Gunnar, J. Am. Chem. Soc. 71, 4158 (1949).

5. Kroll, W. J. and A. W. Schlechten, U.S. Bur. of Mines Infor. Circ., I. C.-7341, p. 5 (1946).

6. Lely, D. and L. Hamburger, Z. anorg. Chem. 87, 209 (1914).

7. Fast, J. D., Philips Technical Review (World Fair Edition), 25 (1939).

8. Kroll, W. J., A. W. Schlechten, and L. A. Yerkes, Trans. Electrochem. Soc. 89, 263 (1946).

9. Kroll, W. J.,A. W. Schlechten, W. R. Carmody, L. A. Yerkes, H. P. Holmes, and H. L. Gilbert, Trans. Electrochem. Soc. 92, 99 (1947).

10. Kroll, W. J., C. T. Anderson, H. P. Holmes, L. A. Yerkes, and H. L. Gilbert, J. Electrochem. Soc. 94, 1 (1948).

11. Lilliendahl, W. C. and H. C. Rentschler, Trans. Electrochem. Soc. 91, 285 (1947).

12. Fast, J. D., Metallwirtschaft 17, 641 (1938). Original not seen. Cited in C. A. 32, 8316 (1938).

13. Lilliendahl, W. C., D. M. Wroughton, and E. D. Gregory, J. Electrochem. Soc. 93, 235 (1948).

14. Ayres, J. A., J. Am. Chem. Soc. 69, 2879 (1947).

15. Eberle, A. R., Atomic Energy Commission Report No. NYOO-2004 (November, 1949).

16. Schmid, P., Z. anorg. allgem. Chem. 167, 369 (1927).

17. Akhrap-Simonova, L. K., Zhur. Priklad. Khimii 11, 941 (1938).

18. Fischer, W. and M. Zumbusch, Z. anorg. Chem. 252, 249 (1944).

19. Unpublished work, L. Abate, Ames Laboratory.

20. Unpublished work, A. S. Ayres, Ames Laboratory.

21. Unpublished work, J. Warf and D. Cline, Iowa State College.

IX. ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. H. A. Wilhelm for his encouragement and counsel, to the members of Metallurgy Group I for their capable and cooperative assistance in the experimental and developmental studies, and to Mr. E. S. Hodge for valuable contributions in metal casting and fabrication. In addition, acknowledgment is made to the members of the spectrographic and chemical analytical groups who, under the direction of Dr. V. A. Fassel and Dr. C. V. Banks, performed the numerous analyses required. Gratitude must be expressed for the funds and facilities made available for the research by the Ames Laboratory of the Atomic Energy Commission.