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A Critical Review of Existing Processes

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Adelaide South Australia

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THE PREPARATION OF SCANDIUM METAL
A Critical Review of Existing Processes

by

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to

SOUTH AUSTRALIAN GOVERNMENT
DEPARTMENT OF MINES

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1. INTRODUCTION

Although scandium was discovered by Nilson in 1879, it has received very little attention until recent years. The scarcity of the element, the difficulties of obtaining it in a pure form, and the absence of any known unique properties are probably the main reasons for this neglect. The only source of scandium known until recently was thortveitite, a scandium-yttrium silicate, occurring in small quantities in Norway and Madagascar. Scandium is, however, widely distributed in nature in very low concentrations, forming about five parts per million of the earth's crust. In recent years the processing of tungsten, uranium, and rare earth ores has yielded concentrates and liquors considerably enriched in scandium and these have provided suitable starting materials for the production of scandium and its compounds.

Recent interest in the rare earth metals and yttrium has prompted the preparation of scandium metal. Scandium is a light metal (2.992 g/cm^3) and has a high melting point (1539°C) and could be a valuable material for incorporation in alloys. Its atomic radius of 1.64Å indicates the possibility of solid solutions with magnesium, titanium, and possibly aluminium, giving alloys with increased strength and ductility and improved high temperature characteristics. The small neutron-capture-cross-section of scandium (24 barns) has made the metal interesting for nuclear reactor technology.

Small amounts of scandium metal have been prepared in several countries for the purpose of studying its properties and its alloying characteristics. This report is a review of the published information on the preparation of scandium metal, as part of a programme sponsored by the South Australian Government Department of Mines for research on scandium. The process liquor of the Port Pirie Uranium Treatment Plant has been shown to be a relatively rich source of scandium. The development of a successful method of extracting the scandium from this source has been described previously.[30]

2. SUMMARY

The known methods of preparation of scandium metal from its halides are reviewed. A brief historical outline of the preparation of the metal is given, and the various methods are then described in detail. The merits of the various processes are discussed, and the most suitable method has been selected for the production of scandium metal as a further extension of this research programme.

3. PREPARATION OF SCANDIUM METAL

Scandium metal was first prepared by Fischer and co-workers[1] in 1937, by electrolysis of scandium chloride in a molten eutectic mixture of lithium and potassium chlorides, using molten zinc as a cathode and collector of the scandium metal produced. The zinc was removed from the

Zn — 2 per cent Sc alloy by vacuum distillation, leaving a product reported to be 94 to 98 per cent scandium, the main impurities being iron and silicon.

Bommer and Hohmann[2] reduced scandium chloride with potassium metal in a glass apparatus and obtained a mixture of the metal and potassium chloride. These workers did not isolate the metal.

During the past few years, scandium metal has been prepared in several countries. Petru[3] and co-workers in Czechoslovakia have prepared the metal in a compact form by the reduction of scandium fluoride or chloride with calcium metal in tantalum and molybdenum crucibles followed by distillation of the product. Spedding[4] and his school in the United States have produced scandium metal by the reduction of scandium fluoride with calcium in tantalum crucibles. The product was vacuum distilled to yield a high purity metal. Another method used by Spedding was to add zinc and lithium fluoride to the scandium fluoride and calcium metal to form a low temperature Sc-Zn alloy and a CaF_2-LiF slag. The reactants needed to be heated only to 1100°C and no vacuum distillation of scandium metal was necessary. A high purity product was obtained. The reduction of the fluoride with lithium metal has also been reported[5]. The metal obtained was of an exceptionally high purity and its microstructure showed it to be essentially free from non-metallic impurity phases.

Two industrial laboratories in the United States, Union Carbide Metals Co. and St. Eloi Corporation, have also prepared scandium metal by the reduction of the fluoride with calcium, the former employing tungsten crucibles and the latter tantalum crucibles. In each case the metal was purified by vacuum sublimation, yielding a product of better than 99 per cent purity.

Spitsyn[6] and co-workers in Russia have prepared scandium metal from the chloride by reduction with calcium at 900°C. The product was cooled, ground to less than 0.2 mm grain size and leached with water and then with caustic soda solution. It was then washed with alcohol, then with ether, and finally dried in a high vacuum. The metal was sintered at 500°C, under a pressure of 100 kg per cm^2., and arc melted to form solid ingots. The product was only 97 per cent pure and a further purification was carried out by vacuum sublimation of the metal.

Achard et al[7] in France obtained scandium metal by the reduction of the fluoride with calcium metal. The addition of an alkaline earth fluoride (e.g. BaF_2) increased the density of the melt. No vacuum sublimation of the metal was carried out but a product of high purity was claimed. The purity of the metal was questioned recently[13].

Iya[8], also in France, has obtained scandium metal by the reduction of anhydrous scandium chloride and scandium fluoride with excess magnesium, forming a scandium-magnesium alloy. Iya also reduced the chloride with calcium in the presence of zinc, obtaining a scandium-zinc alloy. The alloys were then separated by distillation and pure scandium metal obtained. In each case the yield was below 50 per cent.

3.1 The Electrolytic Method

The first recorded preparation of scandium metal was accomplished by the electrolytic method in 1937 by W. Fischer[1].

Fischer used as the starting material scandium chloride prepared by passing a stream of chlorine containing $ScCl_3$ over the oxide in a quartz apparatus heated to 1200°C. The chloride was stored in a sealed quartz tube. The electrolyte was a eutectic mixture of KCl-LiCl; molten zinc was the cathode and collector for the scandium metal produced; the anode was graphite. The electrolytic cell is shown in Figure 1.

The cylindrical vessel (A) was made from electrolytic graphite purified by heating in a stream of chlorine. The crucible (B), of baked magnesia, fitted as closely as possible into crucible (A). Both crucibles were heated in a resistance furnace to a temperature above the melting point of zinc, and crucible (B) was filled with 40 g of high purity zinc, previously distilled under high vacuum in a quartz apparatus. The cathode conductor and stirrer was a tungsten wire (D) of 1 mm diameter which was bent as shown in Figure 1. Tungsten was insoluble in the molten Zn-Sc alloy at the temperature used. Molybdenum could not be used because it was found to be soluble. At 700°C the stirrer (D) was placed in position, protected by the tube of baked magnesia (E) from the fused salts and the anodic chlorine. Ten grams of KCl-LiCl eutectic was melted, the required amount of $ScCl_3$ was added and covered immediately with more KCl-LiCl eutectic. The total charge consisted of 3-5 g of $ScCl_3$, 18 g of KCl, and 15 g of LiCl. When the added salts (F) had become molten, the stirrer (D) was started and the current switched on. With a current of 2-3 amp and a potential of 3-3.5 volts, the electrolysis was continued until about 90 per cent of the scandium was transferred (about 1 hour). During this time the temperature was raised from 700 to 800°C. After electrolysis, the stirrer (D) and the tube (E) were taken out and the cell was left undisturbed at 800°C in the furnace for another 10 minutes before it was put into a desiccator to cool. The additional time in the furnace was necessary to obtain a good separation of metals and salts. After cooling, the graphite and magnesia crucibles were broken up, the metals freed, washed in water and dried in a vacuum desiccator.

In this cell no carbide was formed as the Zn-Sc alloy did not come into contact with the graphite. The highest purity zinc and graphite were used in order to keep the reactants as free as possible from non-volatile impurities. The product contained about 2 per cent scandium with a little potassium and lithium which were easily separated by distillation. The Zn-Sc alloy contained about 0.1 per cent of oxide which could not be removed during the distillation process. The scandium metal was thus enriched in oxygen. This was removed by filtration of the molten Zn-Sc alloy in a narrow cylindrical crucible made from metallic tungsten 10 mm inside diameter and 100 mm long and with a hole 3.5 mm in diameter in the bottom. This tungsten tube, charged with the alloy, was heated inside a quartz tube in a stream of purified hydrogen, care being taken to exclude air and moisture. The molten alloy was collected in a magnesia crucible, the oxide being left in the tungsten crucible. The filtered alloy was then placed in another quartz tube which was evacuated and heated slowly to 1250°C to distil the zinc. Sponge metal was obtained and contained 94-98 per cent of free scandium. The chief impurities were Si 0.3 - 0.5 per cent and Fe 0.2 - 0.5 per cent. No Zn, Mg or W were detected. The melting point was 1450-1400°C.

3.2 The Potassiothermic Method

H. Bommer and E. Hohmann[2] in 1941 prepared scandium metal by the reduction of scandium chloride with potassium metal in a glass apparatus. The potassium metal used for the reduction was purified by repeated distillation in a high vacuum, and sealed in small tubes. The apparatus is shown in Figure 2.

The glass apparatus was dried by heating under a high vacuum. When dry, it was filled with purified and dried nitrogen or argon and a small tube containing potassium was introduced into tube (B). The tip of the small tube was broken off immediately before insertion. Taking care not to admit any air, anhydrous chloride was put through the tube (C) into the position (A) and the tube (C) closed as quickly as possible. (C) and (J) were then sealed off and the apparatus evacuated through (D). The capillary (F) was bent downwards into the position (B^1) by heating and the potassium was distilled slowly from (B^1) into (G).

This distillation eliminated traces of oxide from the metal. Then (F) and (E) were sealed off, a little potassium distilled into the construction (H), and the tube (AF), for the length of (AG), heated to 200-300°C in an electric furnace. After a short time, some of the chloride was reduced, then a little potassium was again distilled into position (H) and the tube put back into the furnace. This stepwise reduction was repeated until the greater part of the chloride was changed into the metal. The last of the potassium was then distilled off, the tube was inverted, and almost the whole length of the tube (AF) put into the furnace. The distillation was then carried out again and the whole procedure repeated several times. As a result of this stepwise reduction with small additions of potassium and the total fusion of small amounts of the reactants, complete reduction took place.

The tube was pulled out of the furnace repeatedly until no mirror deposit of potassium was to be found in the free space between (G) and (H). The individual preparations were reacted at a temperature between 220° and 350°C and formed a loose black powder that did not adhere to the glass walls of the apparatus.

After cooling, the tip (F) was connected with a dry rubber tubing to the vacuum-nitrogen system, and the tip (F) broken off under nitrogen or argon. The alkali metal at (G) served the additional purpose of removing traces of moisture from the rubber tube. The tube at (H) was then broken in order to transfer the mixture of alkali chloride and metal into a nitrogen or argon filled vessel. The scandium metal was not isolated but the powdered mixture was used for analysis and for calorimetric measurements.

3.3 The Calciothermic Method

The reduction of scandium fluoride or chloride with calcium metal is the best established and most common method. The halide is mixed with the calcium and heated in an inert gas atmosphere to 800-900°C to effect the reduction. The slag is separated from the metal, usually by heating above the melting point of scandium. On cooling, the slag forms the upper layer which is easily removed. Volatile impurities such as calcium, are removed by heating under vacuum. The final purification to yield scandium metal of more than 99 per cent purity is by sublimation of the metal under vacuum in tantalum crucibles.

3.3.1 The Czechoslovakian Process

In Czechoslovakia scandium is found associated with tungsten ores, from which it is recovered as a by-product.

According to the published description the scandium was recovered as a fluorosilicate. This product was calcined at 600°C, then mixed with carbon and chlorinated to produce anhydrous scandium chloride. The chloride was reduced with calcium to form scandium metal.[3, 9, 10] The scandium fluoride was prepared from the oxide by the action of hydrofluoric acid.

The apparatus for the reduction and sublimation consisted of an iron ring of 70 mm outer and 30 mm inner diameter. Three molybdenum rods were screwed into the ring and supported a sheet of molybdenum, or a circular ceramic plate, on which the crucibles were placed.

The tantalum crucibles were made from a sheet of tantalum 0.2 mm thick. The bottom of the crucible, 40 mm in diameter and with a rim 5 mm high, was produced by pressing. All joints were spot welded, care being necessary to prevent cracks developing in service. The crucibles were of 40 mm height or more. Good results were also obtained with crucibles of another type which had a molybdenum casing and a pressed tantalum bottom fitted the other way up. Both parts were sealed by spot welding; the crucible mantle was welded by the insertion of a strip of tantalum into the joint.

In some sublimation experiments, molybdenum crucibles were used. They were 40 mm in diameter at the bottom, 60 mm at the top and 20 mm high and were pressed from 0.4 mm thick molybdenum sheet. The tantalum and molybdenum crucibles were fitted with pressed lids of suitable size.

In the experiments with molybdenum crucibles, a second sheet of molybdenum, provided with short legs, supported the crucible. The whole was surrounded with a cylinder made from a molybdenum sheet and fitted with a molybdenum lid. With the larger crucibles, 60-70 mm in diameter, this arrangement was not capable of preventing excessive heat losses.

The tantalum crucibles were resistant to the reactions involved and they remained elastic after repeated use. The molybdenum crucibles usually became brittle after only one reduction run and they were not suitable for reliable experiments.

The complete arrangement was housed beneath a quartz dome 650 mm high and 90 mm in outside diameter placed on a metal flange and made vacuum tight.

A 25 kw high frequency generator was used for induction heating. The heating coil consisted of 10 windings of 110 mm inside diameter and was water cooled. The intensity of heating could be regulated partly by adjusting the coupling and partly by changing the heating coil potential. When using scandium fluoride a mixture of 85 g of scandium fluoride and 50 g of calcium was prepared and packed tightly into a molybdenum crucible. This was placed in the apparatus, which was then evacuated, flushed with argon, again evacuated, and then filled with argon to atmospheric pressure.

Argon was dried before use in concentrated sulphuric acid and was passed over a glowing bed of calcium in a copper tube 1200 mm long, 12 mm inside diameter, and 2 mm in wall thickness. The bed of calcium chips was spread over 200 mm of the tube and heated electrically to 600°C.

The high frequency current of 50 amp was switched on for 1½ minutes raising the temperature to about 850°C measured with an optical pyrometer. A vigorous reaction took place, accompanied by the production of light and heat, during which the current was switched off.

When the reaction was finished, the temperature was raised to 1500°C for 6 minutes. On cooling, the crucible contained a black mass which did not react with water. No metal ingot was obtained. Attempts to separate the reaction mixture by forming a water slurry were unsuccessful, but the separation was accomplished by vacuum sublimation of the scandium.

In experiments with chloride a mixture of 6 g of anhydrous $ScCl_3$ and 2.4 grams of calcium turnings was packed tightly into a small tantalum crucible of 10 mm bottom and 15 mm top diameter and 20 mm high. The mixture was heated in an atmosphere of argon under normal pressure. At 850°C, a vigorous reaction took place, accompanied by the production of smoke. After the reaction ceased, the mixture was heated for 4 minutes with 170 amp. On cooling the crucible contained a white mass of calcium chloride with an even surface and beneath the calcium chloride was a metal ingot, which was separated easily from the tantalum.

Repeated experiments with a bigger charge in a crucible 42 mm in diameter and 50 mm high were unsuccessful. The resulting white reaction mass was permeated with a black sintered product which stuck to the crucible. The black product reacted strongly with water. It contained, very often, large amounts of unreacted calcium. On the bottom of the crucible a small metal ingot was found. The experiment was repeated, a new reaction mixture being added to the ingot and the whole heated to the reaction temperature again. The result was not satisfactory. Hydrochloric acid and some scandium chloride were found in the quartz dome, due probably to absorption of water by the reaction mixture.

In further experiments, lumps of calcium were sliced into chips and then ground in a ball mill immediately before use. To 36 grams of the ground calcium, 100 g of anhydrous scandium chloride was added (i.e. 10 per cent excess) and the mixture milled again. This mixture was much more compact than those used earlier. The charging of the crucible also took only a short time.

Experiments carried out in this way were successful and, after each mechanical separation of the calcium chloride layer, it was possible to add a further reaction mixture to the metal ingot and to repeat the reactions several times. Altogether 70 g of metal was obtained from 288 g of scandium chloride.

The crude scandium metal was purified by vacuum sublimiation from a molybdenum crucible. This process was carried out at 1600°C under a vacuum of 10^{-4} mm Hg. The metal sublimed in 10 minutes and condensed in the form of a coherent silvery mass on the molybdenum lid.

3.3.2 The United States Processes

The calciothermic method of preparing scandium metal has been used in the United States of America, both by Government research establishments and by commercial concerns. Scandium fluoride was used as the starting material and both tantalum and tungsten crucibles have been employed.

The U.S. Atomic Energy Commission's Process. Working at Ames Laboratory, Iowa[4, 5, 11, 12] Spedding, Daane, and co-workers have prepared very pure scandium metal by reducing ScF_3 with calcium metal in tantalum crucibles. The source of scandium was the Norwegian mineral thortveitite.

Scandium is also obtainable as a by-product of the American uranium industry[2a].

The scandium fluoride was prepared by heating scandium oxide to 300°C with a stoicheiometric amount of ammonium bifluoride. The fluoride was sintered at 800°C under a high vacuum to remove any adsorbed gases and to reduce the surface reactivity of the salt. The calcium metal was twice distilled in vacuo. The reactants were mixed to correspond to the following reaction;

$$2\,ScF_3 + 3Ca\ (+\ 10\ \text{per cent excess}) \longrightarrow 3\,CaF_2 + 2Sc$$

The charge was jolt-packed into a tantalum crucible having wall 0.01 inch or thicker, and heated in an induction furnace under a vacuum to about 500°C to remove adsorbed gases. At this temperature, one atmosphere of purified and dried argon was admitted to the furnace and the heating continued to 1550-1600°C. During this heating period, the reaction was observed to begin at about 850°C and to proceed with an even evolution of heat. At the upper temperature the scandium metal and calcium fluoride slag separated cleanly into two layers, the metal forming the lower layer. On cooling, the slag was broken away from the metal, the recovery of which was greater than 95 per cent. At this point the scandium contained 0.5 per cent or more of calcium and from 2 to 5 per cent of tantalum dissolved from the crucible walls. The calcium was removed by maintaining the temperature of the metal at 1550°C in a vacuum for several minutes. The tantalum was present as elemental metal (as opposed to an intermetallic compound) and separation was effected by vacuum distillation of the scandium.

The apparatus employed for vacuum distillation of scandium is shown in Figure 3.

The tantalum crucible extended to within 2 inches of the end of the heated zone of the furnace. The condenser consisted of a sheet of 0.005-inch tantalum wrapped around the crucible and held in place with a band of tantalum wire which extended out of the heated zone. The condenser was capped with a press-fit tantalum lid with a $^1/_8$-inch hole in its centre to allow rapid evacuation of the system at the start. During the distillation the bottom of the crucible was at a temperature of 1650-1700°C, and the top of the condenser was at 800-1000°C. The two collimators were an inch apart, with the lowest one about 2 or 3 inches above the surface of the liquid scandium. These baffles served to direct the vapour to the upper portion of the condenser section, so that the major portion of the condensate was on the underside of the lid. The condensate was a conical, fibrous deposit of bright metal with the tip essentially of fused metal. The compact, partially-fused mass of metal separated readily from the condenser and was consolidated into solid metal by conventional, inert-atmosphere arc melting.

Tantalum was not detectable in the distilled metal which contained the following impurities:

	%
Fe	<0.05
Ca	<0.02
Mg	<0.03
Cr	<0.06
C and N about 100 ppm each	

$<$ - Less than.

Oxygen analysis methods have not been perfected for scandium, but preliminary measurements indicated about 1000 ppm to be present. A volatile scandium oxide may be responsible for the large oxygen content.

The beryllia shields used in the distillation apparatus may be replaced by tantalum radiation shields, and the baffles may have concentric collimating holes instead of the staggered configuration used. At 1650-1700°C the distillation took place at a reasonable rate. By keeping the condenser at 800-1000°C, trace amounts of calcium and magnesium in the feed metal passed out of the still without condensing with the scandium. In a 1-inch diameter still, 25 grams of scandium was condensed in several hours. Higher temperatures employed in an effort to increase the rate of distillation resulted in an increased solubility of tantalum in the liquid metal in the still.

<u>The Union Carbide Metals Co's Process.</u> Dess, Downing, and Heffels[13] from Union Carbide Metals Co., New York, working under a contract for the Unites States Air Force, have prepared 1 pound of scandium metal by reducing the fluoride with calcium metal in tungsten crucibles. It was hoped that tungsten would not dissolve in liquid scandium and that the distillation of scandium would be unnecessary.

The tungsten crucibles were made from tungsten powder by slip-casting and sintering. A typical crucible was slightly conical, about 23 cm high, had an inside diameter of about 9 cm at the top and 7 cm at the bottom, and a wall thickness of about 1 cm, with a slightly greater thickness at the bottom than at the top. The weight of each crucible was between 20 and 24 pounds. Ninety per cent theoretical density was obtained when firing temperatures of 1900°C were maintained for a sufficient length of time. The seamless crucibles were very robust and could be re-used several times, an advantage over thin-walled welded tantalum crucibles which usually became brittle.

Granular calcium was used, comprising particles of which over 90 per cent were between minus 4 and plus 20-mesh. The scandium fluoride and a 10 per cent excess of calcium were weighed and mixed under argon in a dry box. The crucible, plus charge, was heated inductively under argon in a sealed furnace, after preliminary evacuation. The temperature was increased steadily over a period of 60 to 75 minutes to approximately 1300°C, and this temperature maintained for about 15 minutes. The mild reaction between the calcium and the scandium fluoride started between 800 and 850°C. A strongly sintered product of mixed scandium metal and calcium fluoride was obtained. This product adhered only slightly to the walls of the crucible and could be removed easily after cooling. Sintered products from two or three reactions were combined in one crucible and heated above the melting point of scandium (1539°C) in order to obtain a separation of slag and metal. By this technique larger quantities of metal were handled in one crucible and the introduction of impurities from the crucible into the molten scandium was minimized. While the slag layer could be removed without too much difficulty, the ingot of relatively soft scandium metal could be recovered only by breaking the crucible.

In seven operations, over 700 grams of scandium metal was obtained. Some charge was lost during the evacuation of the furnace, and some by absorption into the porous tungsten crucibles. Some scandium metal was also left in the slag, which contained from 1 to 3 per cent of scandium.

The scandium metal contained the following impurities:

	%
Ca	2.1
W	1.36
O	1.0
Fe	0.015
Mg	0.40
N	0.08
H	0.15
Y	0.01
Th	0.01
Ta	0.01
Total	5.135

The high oxygen and hydrogen content was explained by the high oxygen and water content of the original scandium fluoride

(H_2O = 0.52 - 1.31% and O_2 1.5 - 1.8%)

These experiments demonstrated that scandium of 95 per cent purity could be obtained by the direct reduction of ScF_3 with calcium in tungsten crucibles, with yields exceeding 95 per cent, without resorting to vacuum distillation of the metal. Since calcium and magnesium could be removed by vacuum distillation and since oxygen and hydrogen (in the form of H_2O) could be eliminated from the starting materials, scandium of better than 98 per cent purity should be obtainable. Tungsten crucibles were found to be quite suitable and appeared to dissolve in scandium to a lesser extent ($< 2\%$) than tantalum crucibles (2-5%), but the tungsten crucibles must have a low porosity. If the crucibles are made by powder metallurgical techniques such as slip casting, this condition is achieved primarily by sufficiently high sintering temperatures.

The scandium was finally purified by vacuum sublimation.

The apparatus shown in Figure 4 was built inside a vacuum tank. A 50 kw Ajax induction unit was used to supply the power to the induction coil. With the charge at a temperature of about 1550°C, the thermocouple touching the rear side of the condenser plate indicated 1040°C. A temperature region between 1000 and 1100°C was chosen for the following reasons:

1. By the use of a hot condenser, a fractionation could be obtained in one step.
2. The sublimed scandium might not adhere to the crucible or might deposit in the form of a powder if the temperature were too low.
3. At high temperatures (above 1400°C) tantalum reacts rapidly with scandium. The dome on top of the condenser plate was built to function as a condenser for impurities exhibiting higher vapour pressures than scandium and for scandium metal which might by-pass the condenser plate.

The charge consisted of scandium obtained from the calcium reduction of ScF_3 and pieces of the tungsten crucibles known to contain up to 3 per cent scandium. The tungsten was charged in the form of small chips. Since all the material could not be charged at one time, the sublimation of the scandium was carried out in several batches. Successive sublimations were made against the scandium already adhering to the condenser from the previous sublimations in order to deposit large quantities of metal on a relatively small area of condenser. The vacuum during a run was maintained below one micron. At approximately 1550°C about 70 g of scandium metal sublimed within 4 hours.

The scandium condensed in the form of a dense disc about 7 cm in diameter. It was soft, easily machinable, and stable in air, but adhered strongly to the tantalum condenser plate. Three discs totalling 483 g of sublimed metal were obtained. The tantalum could not be removed completely by peeling, and a mixture of 20 parts concentrated HNO_3 and 80 parts concentrated HF was used to remove the last traces. In one case about 15 g of tantalum was removed from a disc of sublimed scandium, only 0.5 g of which was dissolved by the acid treatment.

The sublimed scandium contained, on the average, the undermentioned amounts of the following impurities:

	%
Ta	0.05
Ca	0.01
Fe	0.07
Th	0.05
F	0.08
O	0.3
N	0.01
H	0.3
C	0.03

The high oxygen content could be due to the sublimation of oxygen in the form of an unidentified scandium oxide such as ScO or Sc_2O. The elimination of oxygen in the distilled scandium would therefore require the absence of oxygen in the starting materials. To reduce the tantalum impurities, lower condenser temperatures should be employed, possibly considerably below 1000°C.

The St Eloi Corporation's Process. St Eloi Corporation of Cincinnati, Ohio,[14] has prepared scandium metal of better than 99 per cent purity by the reduction of scandium fluoride with calcium metal in tantalum crucibles and by subsequent vacuum distillation.

The fluoride, produced by dry fluorination of the oxide, was mixed with 10 per cent excess of distilled calcium and reduced in a welded tantalum crucible at 1400°C under nearly 1 atmosphere argon pressure.

To separate the metal from the slag, the temperature was raised to 1650°C, but at this temperature the scandium ingot picked up from 3 to 12 per cent tantalum. The distillation was carried out in a heavy-walled tantalum crucible. The scandium ingot was placed in this container, the assembly evacuated to 0.1 micron and heated to 1600°C. Scandium started to distil at 1550°C and ceased at 1750°C. The product contained about 1 per cent calcium, which was removed by arc melting. The final metal was better than 99 per cent pure and contained very little tantalum.

3.3.3 The Russian Process

Spitsyn, Men'kov, and co-workers[6, 15] have prepared scandium metal of high purity by reducing anhydrous scandium chloride with calcium metal and then purifying the scandium metal by distillation.

Reduction of Anhydrous Chloride. Anhydrous scandium chloride was obtained by chlorinating a mixture of scandium oxide and sugar carbon in a weight ratio of 3 to 1. The chlorination was conducted in a quartz tube at about 1000°C. The $ScCl_3$ sublimed on the cooler parts of the apparatus. This freshly prepared scandium chloride was reduced to metallic scandium at 900°C in an atmosphere of pure argon. The reaction mixture, containing approximately 15 per cent excess of calcium, was placed in a tantalum crucible. The reaction products, which usually contained Ca, CaO, $ScCl_3$ and silicon, were ground to less than 0.2 mm and leached with water, with a 10 per cent solution of NaOH and again with water, and finally with methyl alcohol and ether. In each case the metal was separated by decantation. The resulting powdered metallic scandium was dried in air for 10 to 15 minutes, and afterwards for about 30 minutes in a vacuum (10^{-4} mm Hg).

The metal was pressed into ingots at a pressure of 100 kg per cm^2 while the temperature was maintained at 500-600°C in a high vacuum (10^{-5} to 10^{-6} mm Hg). The ingots were then arc melted in argon.

Analysis showed that the product contained 97-97.5 per cent of metallic scandium, while the total scandium content was 98-99 per cent. Impurities detected were:

	%
Cl	<0.05
Ca	<0.001
Si	0.1
O_2	<0.9
Zr Th Y Yb Fe	<0.1

$<$ = Less than.

Vacuum Distillation of Scandium. The arc-melted metal was purified further by distillation in high vacuum (10^{-5} to 10^{-6} Hg) at 1500-1600°C. Scandium of 99.5 per cent purity was obtained.

The apparatus is shown in Figure 5.

The evaporation of scandium was carried out in a tantalum crucible (1) with a diameter of 30 mm, into which another tantalum crucible (2) was tightly fitted. A third tantalum crucible (3) served as a support for crucible (1) and at the same time as a radiation shield for a tungsten-rhenium thermocouple. High-frequency induction heating was used.

The metallic scandium subjected to sublimation was of 97-97.5 per cent purity. The bulk of the metal (up to 70 per cent) condensed on the lower part of crucible (2), i.e. on a surface whose temperature was only about 300-350°C lower than the temperature of sublimation. This caused significant contamination from tantalum. When separating the sublimate from the tantalum surface, it was necessary to file off a layer of scandium (0.2-0.3 mm) heavily contaminated with tantalum. Scandium obtained in this way was in a compact form with a characteristic silvery lustre and a yellowish tinge. According to analysis it contained 99.5 per cent of metallic scandium. The oxygen content of the sublimate did not exceed 0.1 per cent and the tantalum content was less than 0.05 per cent.

During the sublimation a significant part of scandium (up to 30 per cent) passed through the opening in the crucible (2) and condensed on the water-cooled quartz dome. In this case also, the scandium condensed on the hottest zone and it could be easily removed from the quartz. This product was also of reasonable purity (98.5 per cent), but analysis showed that it contained 0.3 per cent silicon and up to 0.3 per cent oxygen. Evidently a reaction between scandium and silica took place on the surface of the quartz. This fact was borne out by the observation that, after several distillations, the surface of the quartz became uneven.

3.3.4 The French Process

Achard and co-workers[7] in France in 1956 prepared scandium metal by the reduction of scandium fluoride with calcium using an addition of alkaline earth fluorides (e.g. BaF_2) to increase the density of the melt. Fifteen grams of barium fluoride was added to 10 grams of scandium fluoride.

The reactants were pressed together to obtain a compact mass and placed in a cylindrical tantalum crucible. This mass was heated by induction in an argon atmosphere. The reaction was exothermic and continued without external heating until the reduction of scandium fluoride was complete. The temperature was then raised to between 1500 and 1600°C for 5 to 6 minutes to allow the scandium to separate from the slag. Good separation was obtained, though the difference in densities between scandium and flux was small. After cooling and removal of the flux, a compact hemispherical ingot of scandium metal was found and was readily detachable from the tantalum crucible. The scandium obtained by this method was practically free from calcium. Spectroscopic analysis showed about 0.1 per cent of calcium, and total impurities were about 0.2 per cent. The last traces of calcium were eliminated by vacuum fusion at about 1500°C.

The preparation of scandium metal by calciothermy presented several advantages. The fluoride was preferred over the chloride as the latter is difficult to obtain free from oxy-chlorides. The yield of this reaction was excellent, and metallic scandium of 99.8 per cent purity was obtained in a single operation.

3.4 The Zinc Alloy Method

3.4.1 The United States Process

Spedding and co-workers[4] prepared scandium metal by employing a low-temperature process, the reactants being scandium fluoride, calcium, zinc, and lithium fluoride. The zinc formed a low-melting alloy with scandium, and lithium fluoride formed a low-melting $LiF-CaF_2$ slag. This reaction required a temperature of only 1100°C, as compared with the temperature of 1550°C for the reduction with calcium alone. In this way contamination of scandium with tantalum from the crucible walls was avoided, as tantalum reacts rapidly with scandium only at temperatures above 1400°C.

The scandium fluoride was prepared by heating scandium oxide to 300°C with a stoicheiometric amount of ammonium bifluoride, resulting in a 95 per cent conversion. Re-cycling of this material with a small amount of ammonium bi-fluoride effected complete conversion to the fluoride. This was then sintered at 800°C under a high vacuum to remove any adsorbed gases that might be present and to reduce the surface activity of the salt. The zinc used was vacuum melted and of 99.99 per cent purity. Reagent grade lithium fluoride was used after being vacuum melted. The calcium was vacuum distilled twice.

Zinc and lithium fluoride were added to the reaction mixture as follows:

$2ScF_3 + 3Ca + 3Zn + LiF \longrightarrow$ Sc-60% Zn alloy + $3CaF_2$ -LiF (eutectic composition)

A charge consisting of 25 g ScF_3, 16 g Ca, 25 g Zn and 26 g LiF yielded 36 g Sc-Zn alloy and 56 g slag mixture. The reduction and separation of the products into molten metal and slag layers were then possible at 1100°C. The reactants were sealed under an atmosphere of helium by welding in the tantalum crucible, and the crucible in turn was sealed in a helium atmosphere inside a stainless steel bomb. The reaction and subsequent separation of the products into layers was accomplished by heating in a muffle furnace to a temperature of 1100°C. When cool the crucible was opened and the alloy layer was separated from the slag. The bright scandium-zinc alloy, containing 1 to 2 per cent calcium, was brittle and easily crushed into small pieces, which were then heated slowly in an induction furnace under a high vacuum to sublime the zinc and calcium. By avoiding the melting of the alloy, a porous scandium sponge was obtained from which the volatile materials had sublimed completely without splattering. The scandium sponge was arc-melted under a pressure of one atmosphere of argon. An overall yield of 90 per cent usable metal was obtained, with the main loss occurring in vaporization during the arc melting process. The vaporized scandium condensed as a finely divided deposit on the walls of the furnace and could be recovered easily.

Spectrographic analysis of the metal indicated that tantalum, magnesium, calcium, copper, lithium, iron, silicon and zinc were present in trace amounts. Due to the small amount of scandium metal available, no analysis was made for carbon, nitrogen or hydrogen, but the amounts of these impurities were believed to be less than 100 ppm. By analogy to the production of rare earth metals in this manner, the oxygen content was probably about 1000 ppm.

3.4.2 The French Process

Iya[8] in 1956 produced scandium metal by the reduction of anhydrous scandium chloride with calcium in the presence of zinc. The newly-formed scandium metal dissolved in the zinc forming a Sc-Zn alloy. The zinc was later distilled from the alloy, leaving scandium metal, which was consolidated by fusion and purified by vacuum sublimation.

Calcium of 99.99 per cent purity and purified further by vacuum distillation and zinc of 99.99 per cent purity were used. The chloride was prepared from the oxide.

The reactions were carried out in graphite crucibles, lined on the inside with molybdenum foil and containing a disc of molybdenum on the bottom. The crucible was covered with a graphite lid and equipped with a tungsten stirrer. The heating was done electrically and the temperature was measured with a thermocouple. The furnace is shown in Figure 6. Several graphite crucibles were used, the dimensions varying from 70 to 150 mm in height, 25 to 55 mm in inside diameter, 3 to 8.5 mm in wall thickness and 6 to 40 mm in bottom thickness.

Six experiments were carried out, and the best results were obtained with a mixture of 25 grams of calcium, 70.5 grams of zinc and 40 grams of anhydrous scandium chloride. The reduction was carried out in a temperature range of 560 to 620°C and the temperature was raised to 810°C at the end of the reaction. An ingot weighing 54.4 grams, containing 2.5 per cent scandium, and 10.3 grams of granular metal containing 4.5 per cent scandium, were obtained. The yield was 30.5 per cent. An atmosphere of purified argon was employed.

Zinc was removed from the alloy by vacuum distillation in two stages. The first stage consisted of the distillation of part of the zinc, leaving an enriched alloy containing 20 per cent scandium. This was done by heating the alloy in molybdenum crucibles to 600°C under a vacuum of 10^{-3} mm Hg. The furnace was a nichrome-wound silica tube. The final elimination of the zinc and the fusion of the scandium required a temperature of 1500°C. This second stage was carried out in an induction furnace shown in Figure 7.

The outer silica tube had an internal diameter of 120 mm and a height of 600 mm. The metallic support incorporated a window for sighting with an optical pyrometer and a tube which was connected to the vacuum system. Pressures of 10^{-5} mm Hg were obtained. The smaller silica tube had an inner diameter of 75 mm and a height of 500 mm. The tantalum distillation crucible (internal diameter 40 mm, height 50 mm, wall thickness 0.5 mm) and the shield of molybdenum or tantalum (diameter 55 mm, height 100 mm, wall thickness 0.025 mm) were suspended by a tungsten wire in the middle of the inner tube. The disc of silica resting on the top of the inner tube served as a condenser for the zinc. The induction coil was external to the outer silica tube. A high frequency generator delivered 25 kw.

After the apparatus had been outgassed at 1400°C, the alloy was introduced and heated to 600°C when rapid evaporation of the zinc took place. This temperature was maintained for several hours, and then raised to

1400°C for 30 minutes. The furnace was then cooled and pure argon admitted. A layer of shining metal was found adhering strongly to the bottom of the tantalum crucible. The scandium was next vacuum-distilled to yield a product of high purity.

The distillation apparatus was the same as for the distillation of the zinc, but with a molybdenum disc condenser in place of the silica. The position of the shield surrounding the crucible was raised a little to reduce the exposure of the silica tube to the scandium vapour. The distillation was carried out at 1500°C for 1 hour. Some of the scandium vapour attacked the silica. On the tantalum or molybdenum condenser, a brilliant layer of slender crystals was recovered.

3.5 The Magnesium Alloy Method

Iya[8] prepared scandium metal by the reduction of either anhydrous scandium chloride or scandium fluoride with magnesium, producing in each case a scandium-magnesium alloy. The magnesium was later distilled from the alloy and pure scandium metal obtained. The apparatus employed was the same as in the zinc alloy process described above. The reduction was carried out in the same molybdenum-lined graphite crucibles in an atmosphere of purified argon. Several experiments were carried out and the best results were obtained when 146 grams of anhydrous $ScCl_3$ and 109.7 grams of magnesium were reacted at 840-860°C for 60 minutes. From the most successful experiment there was obtained an ingot of 65.5 grams of alloy, containing 14 per cent scandium, and a number of grains totalling 32.5 grams and containing 9 per cent scandium. The total yield was 44.9 per cent.

When the fluoride was reduced with magnesium, the best results were obtained with 188 grams of scandium fluoride and 166.5 grams of magnesium reacting at 840-860°C for 90 minutes. The reactants were stirred, but the stirring was stopped for the last 15 minutes to allow the alloy and the flux to separate. An ingot of 145 grams containing 10 per cent scandium was obtained. The total yield was 35 per cent.

The alloy was heated in the same distillation apparatus as was the the scandium-zinc alloy. Magnesium was distilled at a temperature of 800°C, however, and not at 600°C as was the zinc. The final purification was again done by the sublimation of the scandium itself. The purity of the final product was not given.

4. DISCUSSION

With the exception of the first preparation in 1937, which was done by a fused salt electrolysis technique, scandium metal has always been prepared by the reduction of scandium fluoride or chloride with a metal at an elevated temperature – the thermometallic process. The most widely used method of preparation is the reduction of the fluoride with calcium metal at about 850°C with subsequent vacuum distillation of the metal at about 1600°C to obtain a product of more than 99 per cent purity. The fluoride is preferred to the chloride as it is less hygroscopic and more easily prepared free from oxyhalide.

The alkali metals, lithium and potassium, can be used as reducing agents, but they are difficult to keep free from contamination, so calcium is usually preferred. Inert atmospheres of purified argon or helium are used and the reactants are handled in inert atmosphere glove boxes to keep them free from oxygen, nitrogen, hydrogen, moisture etc. The crucibles are usually made from tantalum. Molybdenum has been used but it is not very satisfactory. Tungsten crucibles are as good or better than tantalum but they are not commonly used because of difficulties in fabrication. Even tantalum and tungsten, however, react with scandium metal above 1400°C, tantalum for example dissolving in the scandium up to 12 per cent or more, depending on the time and temperature of contact. The crucibles are always outgassed, the reactants vacuum-sintered or melted, and the reactions carried out in purified argon or helium, as scandium forms oxides, nitrides, carbides, etc., at elevated temperatures although, at room temperature, scandium is inert to atmospheric gases.

The calciothermic reduction method requires vacuum sublimation of the metal to yield a pure product, because scandium becomes contaminated with the crucible material (tantalum or tungsten) when the reaction mixture is heated above the melting point of scandium (1539°C) in order to separate the scandium metal from the slag, i.e. CaF_2. As sublimation has to be carried out at 1500-1700°C in a vacuum (10^{-4} to 10^{-5} mm Hg) for several hours to obtain about a dozen grams of metal, it is costly, time-consuming and generally undesirable. A process which does avoid vacuum sublimation of scandium is the zinc-alloy process[4], which involves adding zinc to the reactants, i.e. ScF_3 and calcium, and LiF as a flux, so that the scandium may form a low melting point alloy with the zinc. This reduces the minimum temperature required for the metal-slag separation and reduces the contamination of the scandium with the crucible material. The zinc forming the alloy can be distilled at a comparatively low temperature. Greater amounts of reactants are required for the production of the same amount of metal and this increases the difficulty of avoiding contamination.

The electrolytic process suffers from the same disadvantage as the zinc-alloy process since the Zn-Sc alloy contains only 2 per cent scandium and the chloride produces some oxide, so that a pure product is difficult to obtain. The various processes will now be discussed more fully.

4.1 The Electrolytic Method

Scandium chloride was used as the starting material because it has a lower melting point (937°C) than the fluoride (1515°C). The scandium chloride was dissolved in a molten KCl-LiCl eutectic, which was chosen because it has the lowest melting point of the simple alkali chlorides. The scandium chloride has the disadvantage that it is very hygroscopic and difficult to obtain free from oxychlorides, therefore oxygen and moisture have to be rigidly excluded. The scandium chloride was kept in sealed tubes, added to part of the molten electrolyte and then quickly covered up with more electrolyte. Nevertheless the Zn-Sc alloy produced contained 0.1 per cent of oxide. For best results the whole of the electrolytic cell has to be maintained in an inert atmosphere.

The low reduction temperature allowed the cell to be made of graphite with a magnesia lining separating the scandium and zinc from the graphite. This reaction, however, yielded only a zinc-2 per cent scandium alloy. Reactions at temperatures above 800°C could not be used as $ScCl_3$ begins to sublime and the vapour pressures of both the eutectic salts and zinc become appreciable. The use of higher temperatures would also require different container materials.

The filtration technique used to remove the oxide was not completely effective and involved an additional step in the preparation of the metal. The quartz tube used to distil the zinc contaminated the scandium with silicon (up to 0.5 per cent). All the non-volatile impurities in the zinc also finished up in the scandium metal.

This process could be improved by starting with the highest purity zinc possible, preparing the $ScCl_3$ with the least possible moisture and oxygen contents, and placing the electrolytic cell in an inert atmosphere. The distillation of the zinc should be done in tantalum in order to avoid contamination with silicon. These improvements would yield a product of better purity than the one obtained by Fisher (94-98%), but the inherent difficulty of having only a 2 per cent scandium alloy would still remain, with the consequent difficulties of obtaining a really pure product. Alternative electrolyte and cathode materials have been considered by almost all workers engaged in scandium metal preparation, but electrolysis has been discarded in favour of the metallothermic method.

The rare earth metals, which are related to scandium and share many properties in common, have been prepared by the electrolytic method in a state of very high purity. Morrice et al[16] in the United States produced cerium metal of 99.9 per cent purity by the electrolysis of cerium oxide in a fused-fluoride bath (73 per cent CeF_3, 15 per cent LiF, 12 per cent BaF_2). A graphite cell with molybdenum cathodes and graphite anodes was used. It was contained in a glove box in which the temperature pressure and composition of the atmosphere were controlled. The reaction temperature was 810-830°C, and the rate of production of cerium metal was about 0.8 pounds per hour. The electrolysis was continued for about 2 hours until massive nodules of cerium bridged the gaps between the anodes and cathodes. The electrolyte was allowed to solidify within the cell atmosphere and, when cold, was removed from the cell box. It was then broken up to recover the cerium nodules. The current efficiency was 85 per cent. High purity lanthanum metal was also produced by Morrice et al[17] by the electrolysis of La_2O_3 in a LaF_3-LiF-BaF_2 bath at 950°C using a similar technique. The total impurity was 0.1 - 0.2 per cent.

The electrolytic method is in fact very successful in producing most of the rare earth metals[18]. By analogy it should be possible to prepare scandium metal by electrolysis. This electrolytic method has an advantage over the metallothermic process in that the starting material is the oxide and not the halide. Since scandium halide is prepared from the oxide, the electrolytic method would eliminate one step in the preparation. The cell, however, has to be contained in an inert atmosphere glove box, involving costly equipment, and, since the method has not been proven for scandium, it would entail some experimental work before satisfactory results could be expected.

4.2 The Potassiothermic Method

Bommer and Hohmann[2] have been the only workers to prepare scandium by the reduction of $ScCl_3$ with potassium.

The reaction products could not be separated by fusion as glass apparatus was used and the melting point of scandium is 1539°C. Even if tantalum or tungsten crucibles were used, separation by fusion would be difficult since KCl boils below the melting point of scandium metal. Using ScF_3 instead of $ScCl_3$ would not alter the problem, as KF has the same melting point as KCl. Separating the products by distilling the KCl and leaving the scandium behind should be possible, but the high temperature of distillation would result in the contamination of the scandium with the crucible material. A possible way of obtaining pure scandium by this method would be to separate the products by dissolving the KCl in water, drying the scandium powder and consolidating it by sintering under pressure and by arc melting. A similar method has been used by Spitsyn[15] in Russia, but utilising calcium instead of potassium. Spitsyn's scandium was not very pure and vacuum distillation of the metal was still necessary in order to obtain a product of better than 99 per cent purity.

4.3 The Calciothermic Method

The reduction of scandium halides with calcium metal is the most widely practised technique. It is relatively simple and yields a metal of reasonable purity. To produce scandium of high purity, however, requires vacuum sublimation of the metal itself.

During the last 7 or 8 years, the process has been successfully applied in several countries. It requires tantalum or tungsten crucibles, a temperature up to 1600°C and an inert atmosphere. The reaction is exothermic and supports itself without becoming violent. The slag and scandium metal can be separated easily, though the metal often adheres to the crucible. The reactants and crucible have to be outgassed carefully to eliminate oxygen and moisture. High frequency induction furnaces have been used invariably for heating and, although other alkaline or alkali metals could be used as reductants instead of calcium, the latter is preferred as it is less reactive.

4.3.1 The Czechoslovakian Process

In Petru's experiment [9,10] in which scandium fluoride was used, separation was not satisfactory as the highest temperature (1500°C) was below the melting point of scandium (1539°C) so that no segregation was achieved. Also, as calcium fluoride is insoluble, aqueous leaching was likewise unsatisfactory. Heating above the melting point of the scandium should have resulted in good separation. This experiment also showed that molybdenum was not a satisfactory crucible material.

The reduction of $ScCl_3$ was carried out in tantalum crucibles. In early experiments the reactants picked up a considerable amount of moisture and hydrochloric acid was formed. In later experiments great care was taken to exclude moisture and oxygen. These experiments were successful and 70 grams of scandium was prepared, containing, it was claimed, a metal of 99 per cent purity. The scandium ingot was stated to be easily separable from the tantalum crucible. Other workers have found that scandium adheres to the crucible walls.

The reactants were not added in stoicheiometric amounts but with 10 per cent excess of $ScCl_3$. This was unusual as all other workers have added 5-10 per cent excess of calcium. The amounts added are probably of little consequence with the chloride, as any $ScCl_3$ left after the reduction can be distilled, removed with the slag or dissolved with water. In any case the addition of excess of scandium halides is wasteful, as they are of greater value than calcium metal.

After the reaction, the charge was heated above the melting point of scandium and should, therefore[4], have picked up a considerable amount of tantalum. No analysis for tantalum was given and 99 per cent purity was claimed. No values for non-metallic impurities were stated, and it appears rather doubtful that such high purity metal could have been obtained without vacuum sublimation of the scandium. The vacuum-sublimed samples, were probably of 99 per cent purity or better.

4.3.2 The United States Processes

In the three processes described, scandium was prepared by the reduction of the fluoride with calcium. All three producers used 10 per cent excess calcium for the reduction, and all reported that the product contained calcium which they eliminated by heating under vacuum. They all reported the reaction as exothermic but not violent. A slow rate of heating was employed. All took great care to eliminate moisture and adsorbed gases, and all carried out the reduction under about one atmosphere pressure of argon. Spedding[4] and the St Eloi workers[14] used tantalum for crucibles and Dess et al[13] used tungsten. The latter was superior but the crucibles had to be carefully fabricated. However, in all cases, their products were contaminated with crucible material and vacuum sublimation of scandium was resorted to as a final purification step. Good separations of metal from slag were reported, but the scandium ingot adhered to the crucible walls. Yields of over 95 per cent were obtained.

Similar distillation apparatus was used by the three scandium producers with differences only in minor details. All used induction heating and tantalum crucibles. Spedding obtained a metal containing no tantalum and less than 0.02 per cent calcium.

Dess found that his product contained 0.05 per cent tantalum, and he recommended condensation temperatures below 1000°C.

The St Eloi Corporation used a slightly different still but, due to the low condenser temperature, their product contained about 1 per cent of calcium, which was removed during the final arc melting process.

All workers obtained a product of more than 99 per cent purity, with oxygen as the main impurity (about 1000 ppm). The oxygen cannot be eliminated by vacuum distillation of the metal and the only way to reduce it is to eliminate it as far as possible from the starting materials and the furnace atmosphere.

The vacuum distillation of the scandium metal is in general an expensive and time-consuming step requiring temperatures above 1550°C for a period of hours, tantalum crucibles and condensers and a high vacuum. The procedure invariably leads to some loss of scandium. Therefore, a process which could eliminate vacuum distillation would have a decided advantage.

4.3.3 The Russian Process

The process described by Spitsyn et al[6, 15] has some advantages over the American method in that temperatures of 900°C only were employed, no contamination of scandium with crucible material was encountered, and no sticking of scandium metal to the crucible occurred, so that the same crucible could be used repeatedly, and no induction heating was required.

On the other hand the chloride is difficult to obtain free from oxy-chlorides. According to Spitsyn[15], scandium, though not reactive with oxygen at room temperature, is covered by an oxide film about 600A thick which forms in 170 hours at 20°C. Thus it may be difficult to obtain a high purity product by this method, and Spitsyn had to resort to vacuum sublimation to obtain scandium of 99.5 per cent purity. If a clean enough product could be obtained without vacuum sublimation of the scandium, the process would be very attractive.

4.3.4 The French Process

The method described by Achard and co-workers[7] was identical with the American method except for the addition of the BaF_2. This addition, however, was probably superfluous as a clean metal-slag separation takes place without it. The presence of BaF_2 only increased the bulk of the reactants, necessitating larger crucibles and introducing additional impurities. Achard reported that the scandium ingot was easily detached from the tantalum crucible, in contradistinction with other workers who found scandium to adhere to the crucible. The scandium was also reported as practically free from calcium (0.1%), and with a total impurity of 0.2 per cent. No vacuum sublimation of the scandium was done and the yields were reported as excellent.

The production of 99.8 per cent purity scandium by this method without vacuum distillation is improbable, and has been questioned by several workers (e.g. Dess[13]). Firstly, no analysis was made of the non-metallic impurities and, secondly, the density was given as 3.3 g cm^{-3}, which is

10 per cent higher than the value reported by other workers,[4,15,19] suggesting that the high density may be due to several per cent of tantalum impurity. To obtain a really pure product, therefore, vacuum sublimation has to be resorted to. Furthermore the process shows no advantages over the usual fluoride reduction method. On the contrary, the superfluous addition of BaF_2 makes it less attractive.

4.4 The Zinc Alloy Method

The advantage of the method of Spedding et al[4] over direct fluoride reduction is that the reactants have to be heated only to 1100°C in order to obtain a metal-slag separation. The scandium-60 per cent zinc alloy was easily separated from the slag and the crucible. The zinc and excess calcium were removed readily under vacuum. The scandium contained only trace amounts of tantalum as the temperature during the entire preparation never exceeded 1200°C. Therefore no vacuum distillation of scandium was necessary in order to prepare a metal of more then 99 per cent purity.

One disadvantage of this process is that the bulk of the reactants is three times greater than in the direct reduction method. Larger crucibles are required and the introduction of additional impurities from the extra reagents is an extra hazard.

Iya[8] employing a zinc alloy process used $ScCl_3$ instead of ScF_3. the low yield and the low scandium content in the alloy could have been due to the low temperatures used and the presence of moisture and oxygen in the system. Petru[10] reported poor results in his initial chloride reductions until he took great care to exclude moisture and oxygen, when his results improved remarkably. Hence higher temperatures and rigid exclusion of reactive gases would probably have resulted in much better yields and greater scandium concentrations in the alloy.

Iya's method would be of advantage, since it does not require LiF as Spedding's method does, provided a greater yield and a better scandium concentration in the alloy could be obtained with sufficient purity to make the vacuum distillation of scandium unnecessary. Otherwise Spedding's method or the direct reduction process is to be preferred. Heffels[13,20] obtained alloys containing up to 12.4 per cent scandium, with yields of 66 per cent. The higher yields and concentration of scandium in the alloy were probably due to the higher temperatures obtained by the boosting effect from the reaction of the $ZnCl_2$ with calcium. This indicates that higher concentrations and yields should also be possible with Iya's method, if higher temperatures were employed.

4.5 The Magnesium Alloy Method

Iya's work described in section 3.5 produced an alloy in ingot form and two thirds of the metal was contained in the 14 per cent Sc alloy. Heffels[20] also studied the reduction of $ScCl_3$ with magnesium and reported no separation between the Sc-Mg alloy and the $MgCl_2$ slag. The density differences between the metal and the slag are small, and slight variations in impurities (e.g. container material) and alloy composition might be decisive for the metal-slag separation, if a separation is obtainable at all.

Iya also reported the preparation of Mg-Sc alloys containing up to 10 per cent scandium in the alloy and yields of 35 per cent scandium by the reduction of ScF_3 with excessive amounts of magnesium. Following a method successfully used by Carlson and co-workers[21] in the preparation of yttrium metal, Dess[13] tried unsuccessfully to obtain a Sc-Mg alloy by the reduction of ScF_3 in the presence of magnesium as alloying agent and $CaCl_2$ to reduce the melting point of the slag. He hoped that a low melting high Sc-Mg alloy could be obtained at temperatures low enough to minimise the introduction of impurities from the tantalum container. However, no melting of the metal could be obtained at temperatures up to about 1400°C. Since it was known that scandium would be contaminated by tantalum at higher temperatures, Dess did not pursue this line any further.

Thus the direct reduction of scandium halides with magnesium, which would also function as an alloying agent, is not very promising.

5. CONCLUSIONS AND RECOMMENDATIONS

Scandium metal was first prepared by electrolysis in 1937[1], but the electrolytic method has not been used for scandium metal production since, although it is the standard method for the preparation of rare earth metals and aluminium which share many properties in common with scandium.

The second scandium preparation method used was the reduction of anhydrous $ScCl_3$ with potassium[2]. The separation of the metal from the KCl during the reduction was not accomplished, however, and as this may be difficult if not impossible, the method has not been repeated. The standard and most successful method for the preparation of scandium metal of more than 99 per cent purity is the reduction of ScF_3 or $ScCl_3$ with calcium at about 850°C. Usually the fluoride is used as it is not hygroscopic and is more easily prepared free from oxyhalides. This method, however, requires high temperatures (above 1550°C) in order to melt the scandium and to obtain a metal-slag separation, as well as to distil the metal. The only suitable crucible materials are tantalum and tungsten, though even these materials dissolve to some extent in liquid scandium.

The scandium halides have also been reduced with lithium metal[5] instead of calcium, yielding better results, but, owing to the greater difficulty of handling the lithium, calcium is usually preferred. Magnesium has also been used as a reductant and at the same time as an alloying agent, with the hope that a low melting alloy of Sc-Mg would form, enabling lower temperatures to be employed[8,20]. This method was only partially successful, and it is not used at present. A more successful method is to reduce the fluoride with calcium in the presence of zinc as an alloying agent[4,8]. High purity metal has been prepared in this way without vacuum distillation of the scandium because, at the lower temperature employed, the crucible material (tantalum or tungsten) does not dissolve in scandium. A more novel approach is to reduce the chloride with calcium at 900°C and to obtain a metal-slag separation by dissolving the $CaCl_2$ with water[15]. Rather impure metal, however, was obtained and vacuum sublimation had to be resorted to. Thus several methods for the preparation of scandium metal are available and the one actually chosen may depend on the equipment and reagents available. Slight variations of these methods are also possible.

The reduction of scandium fluoride with calcium, followed by vacuum distillation, is the most widely used method, therefore it is recommended as the standard and safe process. If high temperature vacuum distillation is to be avoided, Spedding's zinc alloy method[4] would be the next choice. However, one may with profit try several variations of the established methods in order to simplify the processes and to obtain a purer product. One such method is the reduction of the fluoride with lithium metal instead of calcium. Lithium has a much lower melting point (179°C) than calcium (846°C) and, therefore, need not be ground and mixed with the fluoride, but can be added in large lumps. This reduced handling should lower the oxygen pick-up by the lithium metal and hence increase the purity of the scandium. Another possible advantage is that the separation of the metal and the slag may take place at a lower temperature with lithium than with the calcium reduction method. When calcium serves as the reductant, the charge has to be heated above the melting point of scandium (1539°C) to obtain the metal-slag separation, since CaF_2 melts at 1360°C and the densities of CaF_2 and scandium are very similar. With the lithium reduction, the LiF formed has a density of 2.3 g cm^{-3}, compared with 2.99 g cm^{-3} for scandium, and the melting point of LiF is only 870°C, therefore a separation of the metal and slag may take place below the melting point of scandium, possibly at less than 1400°C, a temperature below which tantalum does not react readily with scandium. Hence no vacuum distillation of scandium would be required, since this is employed chiefly to separate the tantalum impurity from the scandium. The lithium reduction method would therefore not only lead to a purer product (less oxygen, etc) but it would also dispense with the vacuum distillation which is a very expensive and time-consuming process. However, greater precautions would be required in handling lithium metal than are necessary with calcium.

If in the lithium reduction method the metal-slag separation could not be accomplished below the melting point of scandium and vacuum distillation had to be employed to eliminate the tantalum impurity, Spedding's zinc alloy method could be modified to yield another simplified process. The scandium fluoride could be reduced with lithium instead of calcium in the presence of zinc to form a low melting alloy. The addition of LiF to lower the melting point of the CaF_2 slag would be unnecessary, as the slag would in this case be LiF itself. Thus the same result could be achieved at a lower temperature without the addition of LiF simply by substituting lithium for calcium as the reducing agent. The lithium would again be used in lump form, as could the zinc, since it melts at 410°C, a temperature that is far below the reduction temperature ($\sim$ 850°C).

An alternative method to the fluoride reduction with lithium is the reduction of the chloride which was used by Block and associates[22] in the preparation of yttrium metal. After the reduction, the slag, LiCl and some lithium, was removed from the yttrium metal by keeping the products at 900^0 under vacuum for several hours, when the LiCl and lithium distilled off, leaving an yttrium sponge. At this temperature no contamination of the metal with the crucible material took place, hence no vacuum distillation of the metal was required. The same method could be applied to scandium, the only disadvantage being that the $ScCl_3$ is difficult to prepare free from oxychlorides and that it is hygroscopic, requiring a dry atmosphere at all times. If pure and dry $ScCl_3$ were available, this method would be useful. Another possibility with the chloride is to dissolve the LiCl slag in water as LiCl is quite soluble. This method was used by Spitsyn[6,15], but a metal below 99 per cent purity was obtained. Since in all the methods discussed above the purity of the final product depends on the purity of the reactants (especially with regard to oxygen content), great care must be exercised in preparing and handling the starting materials. The weighing and mixing of the reagents must be conducted in inert atmosphere glove boxes (using dry and purified argon or helium). The crucible and furnace should be outgassed and refilled with inert dry gas before charging. The scandium halides should also be outgassed and possibly sintered to reduce their surface reactivity. The reducing metal, lithium or calcium, should be vacuum-melted and vacuum-distilled or, if very pure metal ingots are available, they should be taken out of their containers in an inert atmosphere dry box, and put straight into the outgassed crucible,after removal of their outer layers. The charged crucible should be transferred as quickly as possible into the furnace, the reactor outgassed again at about 500^0C, and filled with dry and purified argon to atmospheric or nearly atmospheric pressure. The crucible should be covered or sealed, and the heating should be done slowly to allow plenty of time for the reaction to go to completion. With the direct reduction method, the charge should be heated above the melting point of scandium for a few minutes to allow a metal-slag separation to take place, and then cooled and the slag separated mechanically. The scandium ingot should then be broken up into small pieces and heated very slowly to several hundred degrees under vacuum to evaporate the volatile impurities, or the zinc if the zinc alloy process is used. The metal should finally be melted under vacuum.

The non-volatile impurities, such as tantalum and tungsten, can be separated by distilling the scandium metal itself. Oxygen, however, cannot be eliminated effectively by either distillation or vacuum melting, and it usually forms the main impurity in the scandium metal (about 1000 ppm). But oxygen has been reduced to 150 ppm in yttrium metal by Carlson et al[21] using a fused salt extraction technique. Carlson reduced YF_3 with calcium, in the presence of magnesium to form a Y-Mg alloy, and with the addition of $CaCl_2$ to form a CaF_2-$CaCl_2$ slag. The Y-Mg alloy was purified by adding to it $CaCl_2$ containing YF_3 or YCl_3 and heating to 950^0C. The fused salt-alloy mixture was stirred for 30 minutes. Oxygen was removed by the YF_3-$CaCl_2$ mixture, and both oxygen and fluorine were extracted by fused YCl_3; the fluoride content was also lowered substantially by contact with $CaCl_2$.

The purest metal was obtained by extracting with YF_3-$CaCl_2$, followed by a second extraction with YCl_3. Fluorine was also removed by electron beam melting and zone refining of yttrium metal, but oxygen could not be removed by these means. A similar purification process should likewise work for scandium, though this is not reported in the literature.

The scandium metal obtained is usually in the form of crystals (from vacuum sublimation) or a metallic sponge (from the alloy process). It has to be consolidated, therefore, into solid ingots. This is usually done by arc melting under argon, using a nonconsumable tungsten electrode and a water-cooled copper hearth[15], or the metal is pressed into electrodes for consumable arc melting. This involves some loss of the metal as the vapour pressure of scandium is sufficiently high for about 10 per cent of the metal to evaporate and condense around the inside of the furnace as "fog". This metal however is easily recovered[4,12,23].

The pure scandium metal has a silvery lustre with a slight yellowish tinge; it is quite soft and is sufficiently ductile to be rolled into thin sheets without annealing. Its structure is hexagonal. There is no apparent reaction of scandium metal with air at room temperature, even on standing for long periods of time. Spitsyn[15] reported that the metal formed an oxide film of about 600 Angstrom units after exposure to air for 170 hours at 20°C. Longer exposures did not result in any increased oxidation. The similarity to aluminium is evident. Noticeable oxidation started at 250°C and became rapid at higher temperatures. At such temperatures scandium reacts also with nitrogen, carbon and other common elements. The properties of the metal have been reported by a number of workers[4,11,12,15,19,23-28].

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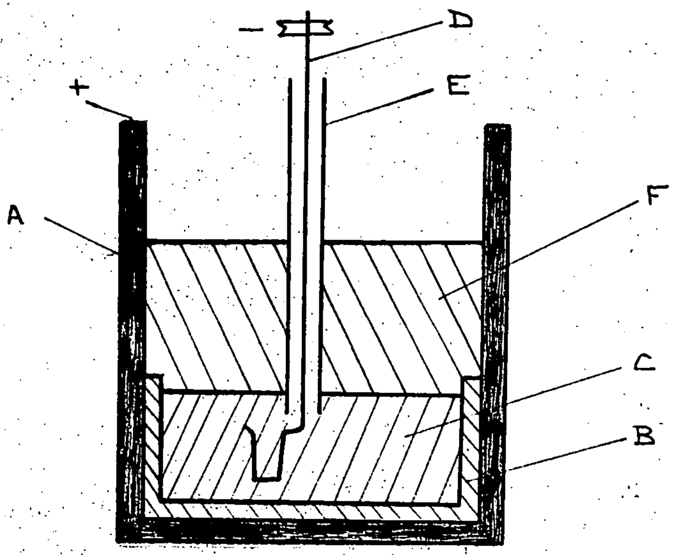
FIGURE 1.



A = graphite crucible,

B = MgO crucible

C = Zn-Sc alloy,

D = tungsten wire,

E = MgO tube ,

F = KCl-LiCl-$ScCl_3$ fused salts.

FIGURE 2.

APPARATUS FOR THE PREPARATION OF SCANDIUM METAL

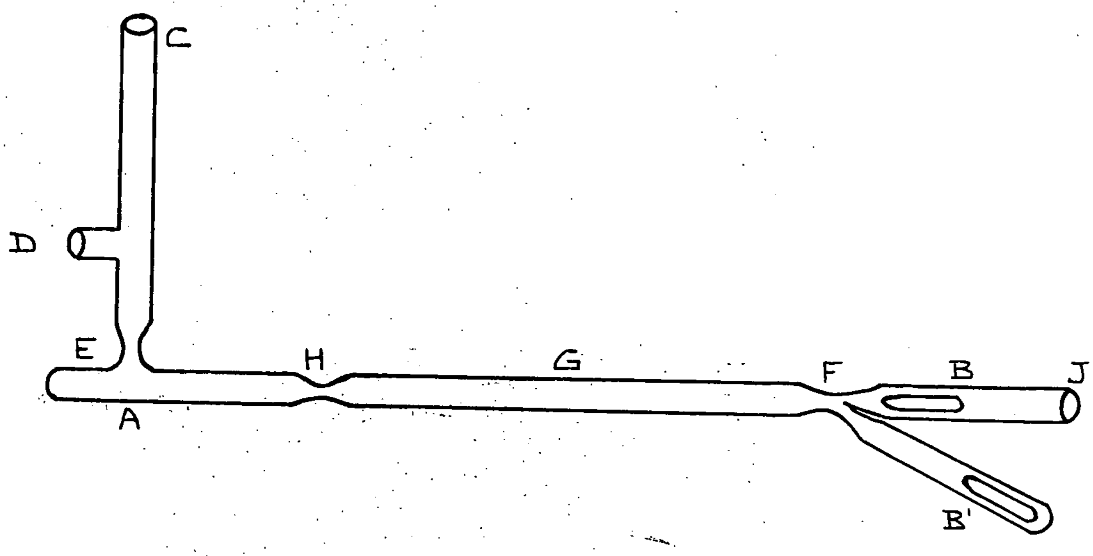


FIGURE 3.

APPARATUS FOR DISTILLING SCANDIUM

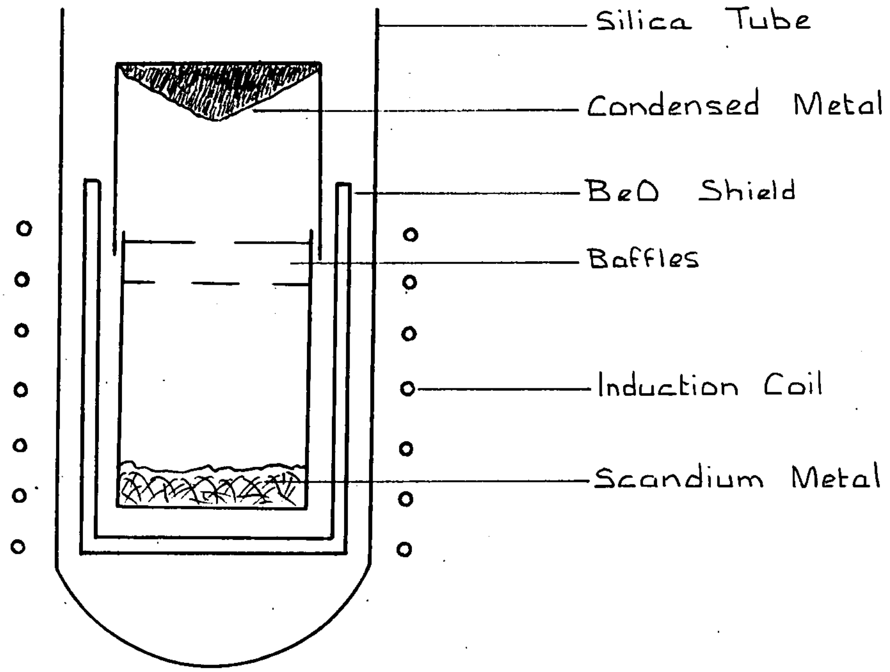


FIGURE 4.

APPARATUS FOR SUBLIMATION OF SCANDIUM

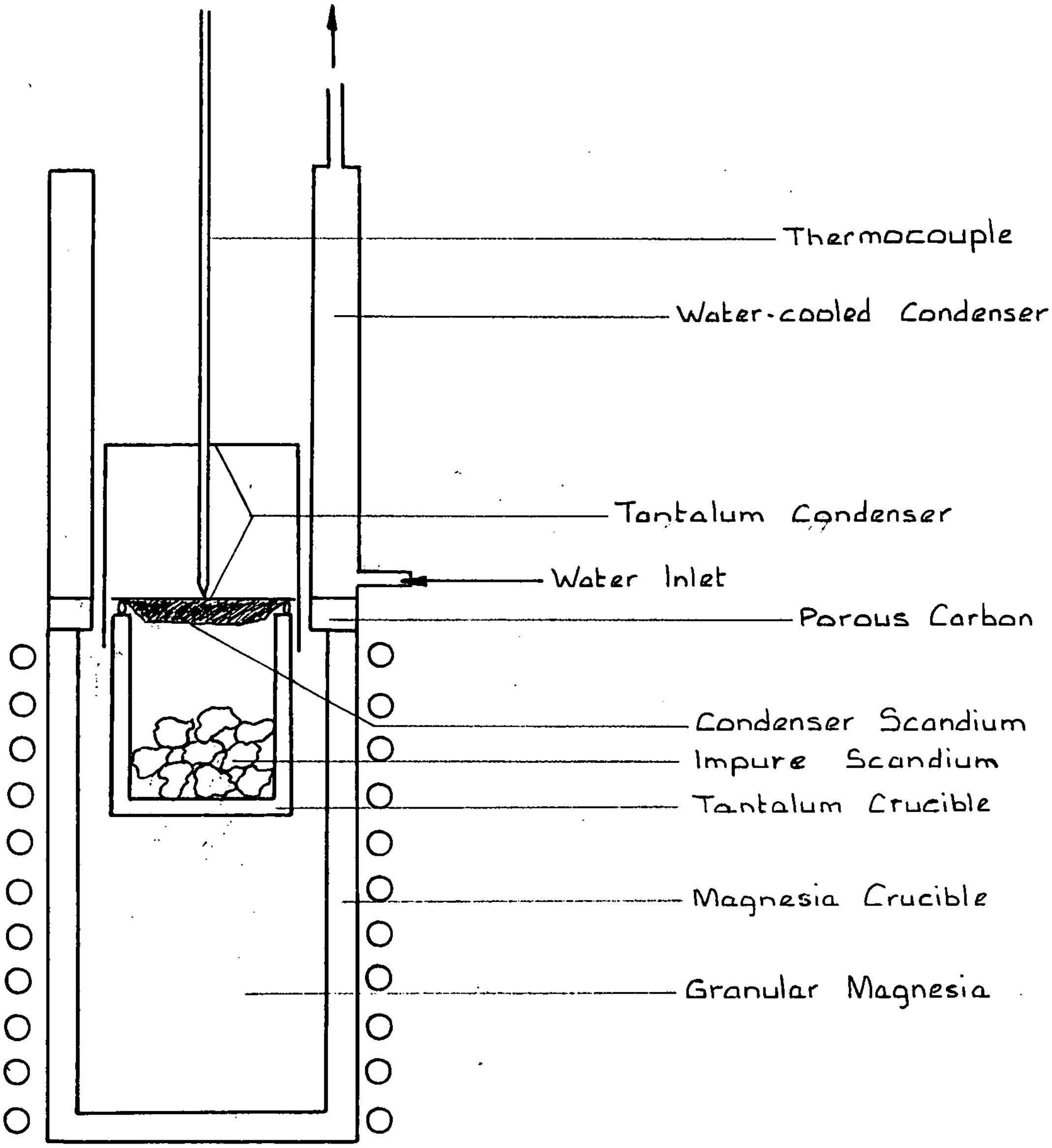
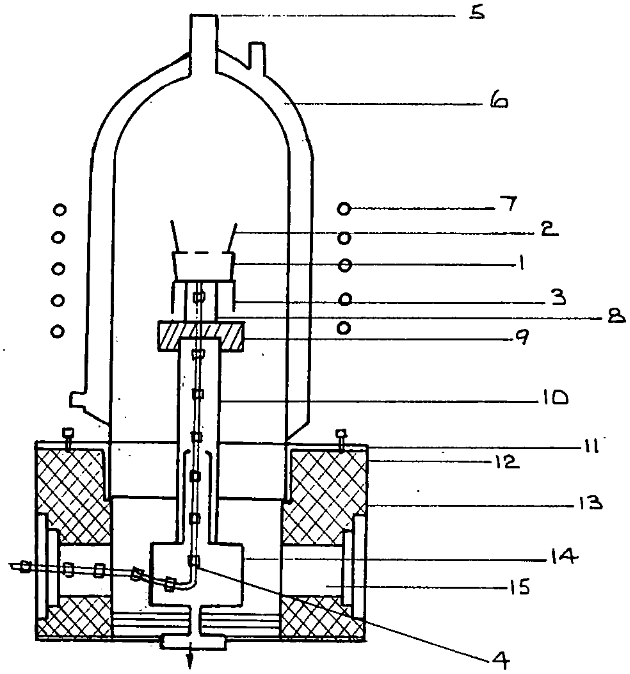


FIGURE 5.

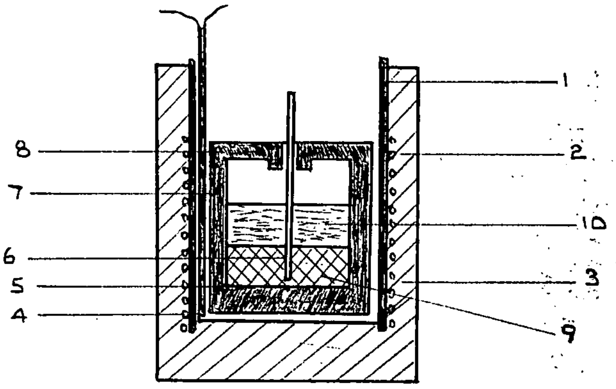
HIGH VACUUM APPARATUS FOR DISTILLING SCANDIUM METAL



1. Evaporating crucible	9. Molybdenum support
2. Condenser	10. Ceramic tube
3. Radiation shield for thermocouple	11. Flange
4. W- Re thermocouple	12. Rubber seal
5. Optic glass for pyrometer	13. Brass stand to diffusion pump
6. Water-cooled quartz dome	14. Stand for ceramic tube
7. Induction coil	15. Opening in brass support for thermocouple
8. Tungsten support	

FIGURE 6.

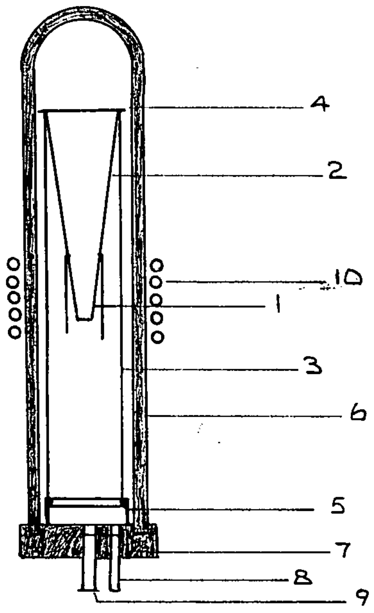
REDUCTION FURNACE



1.	Silica tube	6.	Tungsten stirrer
2.	Nichrome wire	7.	Graphite crucible
3.	Fire bricks	8.	Graphite cover
4.	Thermo-couple	9.	Alloy
5.	Molybdenum disc	10.	Flux

FIGURE 7.

ZINC DISTILLATION FURNACE



1. Tantalum crucible	6. Exterior silica tube
2. Tungsten wire	7. Cooling
3. Interior silica tube	8. Vacuum line
4. Silica disc	9. Pyrometer window
5. Metallic support	10. Induction coil.