Ultrapurification of Refractory Metals

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INTRODUCTION

Refractory metals (m.p. > 1875 °C) of commercial interest are transition elements belonging to groups IVa (Hf), Va (V, Nb, Ta) and VIa (Mo, W) of the periodic table of elements, in which the inner shells (d-shells) of succeeding elements become more complete. These refractory metals offer utilization by virtue of the characteristic structure (strong lattice) in several advancing technologies; atomic energy, aerospace, electronic and process industries. The credibility of their extensive and varied applications is on account of high m.p., great hardness and resistance to corrosion and the ability to form innumerable invaluable ferrous and non-ferrous high temperature and superalloys.

The useful engineering properties of these refractory metals are drastically influenced by the presence of even low levels of both metallic and interstitial impurities. For any application, it is important to have a knowledge of the degree of purity as well as the types of impurities associated with the refractory metals. Efforts to refine refractory metals have made available to the fabricators a host of materials having better ductility, low ductile-to-brittle transition temperature (DBTT) and crystallisation temperature as well as easier formability, machinability and weldability. Ultra high purity metals are also becoming increasingly important in physical studies of structure-property relationship which have contributed substantially towards developing new high temperature structural materials. Of special mention are the ultra-high purity refractory metals like Nb, Ta, Mo and W, whose silicides have great potential for very large scale integration (VLSI) applications /1,2/. For use in the microelectronic device fabrication, the impurities of α emitter type (U, Th) in these metals should be at ppb level.

The ever increasing demand of high purity refractory metals has side by side resulted in the study and development of new and improved methods of preparation, refining, ultra purification and single crystal growth and procedures for meticulous handling of materials during synthesis. Also the crucial and pervasive needs to improve techniques for complete and unambiguous analysis of very low trace levels of impurities and characterisation have been an on-going process and has yielded, in conjunction with the use of lasers and other means of exciting specimens, the analytical techniques that are more sensitive and selective.

Obtaining of pure refractory metals is different than other metals. The trace removal of impurities (both metallic and interstitial) from refractory metals is rendered extremely formidable because of their high affinity for hydrogen, oxygen, nitrogen and carbon at elevated temperatures. While the trace metallic impurities (of natural origin, picked up during processing) from the refractory metals are removable by several refining processes like electrolysis, iodide process, vacuum distillation and zone refining, the trace interstitial impurities removal is accomplishable by special techniques such as induction melting, levitation melting, electron beam melting, electromigration and solid state deoxidation. The growth of single crystals of refractory metals required for studying basic properties is a very involved work mainly because of high m.p. of the metals necessitating the employment of crucible- or containerless melting techniques.

The present paper deals with the purification processes employed for obtaining high purity refractory metals, namely Hf, V, Nb, Ta, Mo and W. Starting normally from the commercial grade metals further refining processes such as pyrovacuum melting, fused-salt electrolysis, iodide process (van-Arkel de Boer), zone refining and electrotransport are described. Most purification schemes warrant the use of processes in combination since no single process is adequate for purifying all metals or removing all types of impurities. In this presentation, process schemes adopted for most satisfactory metallurgical purification are also included metal-by-metal.

Prior to chemical analysis of a metal (or an intermediate product), it is imperative to have a knowledge of the degree of purity that is necessary and the acceptable limits of various trace impurities present for the end application of the refractory metal. Assessment of refractory metals for the presence of ultra trace elements is done by applying analytical techniques such as emission spectroscopy (ES), mass spectroscopy (MS), neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS) and vacuum fusion or extraction. Perhaps the most convenient and also rapid method of purity assessment, though indirect, of refractory metals is by determining the electrical resistance ratio (RR) at room temperature (298K) to that at liquid helium temperature (4.2K). The RR method is a common means of comparing the quality of high purity metals produced either by improved processes or by different routes. The general physical properties and the highest resistance (RR) values reported for various high purity refractory metals in the literature are shown in Table 1. Though in the majority of cases, the RR values cited in the literature are accompanied by the respective chemical compositions determined by other trace analytical methods, the highest reported RR values for several metals are not necessarily supplemented by the chemical analytical data.

ULTRAPURIFICATION TECHNIQUES

The refractory metals (crude) produced after the so-called separation methods constituting an extraction flow sheet are further purified by various refining processes. These processes utilise the difference in physical, chemical or electrochemical behaviour of impurities in the refined and the crude metal. Better utilisation of a refining process can be affected by successive operations. For ultrapurification of refractory metals, the processes which are successfully employed are (i) pyrovacuum treatment for removal of volatile impurities, last traces of gases and carbon, (ii) fused salt electrolysis, (iii) iodide refining (vapour phase decomposition), (iv) zone refining and (v) electrotransport.

There is no royal road to achieve ultrapurification of refractory metals. The choice of a method for ultrapurification depends in the first place on the types and extent of impurities present in the starting material; knowledge of the origin and processing history of the material is a prerequisite, since all purification processes are based on the difference in reactivity of the host material and impurities to a given treatment. Other

TABLE 1
PHYSICAL PROPERTIES OF REFRACTORY METALS

(including highest RR value reported to date)

Properties	Hf	V	Nb	Ta	Mo	W
At. No.	72	23	41	73	42	74
At. Wt.	178.49	50.942	92.986	100.948	95.94	183.85
Crystal structure	Hex	B.C.C.	B.C.C.	B.C.C	B.C.C	B.C.C
Lattice constant(s) a_0	0.3196-7	0.3026	0.33004	0.33026	0.31469	0.31648
(nm) C_0	0.50578					
Density (g.cm-3)	13.28	6.11	8.57	16.6	10.22	19.254
M.P.(°C)	2222	1890	2468	2996	2610	3410
B.P.(°C)	4602	3380	4742	5425	3612	5660
RR value (highest)	5000	2000	20680	7000	3x105	
(ref)	(74)	(19)	(21)	(124)	(75)	(176)

important considerations for keeping the integrity of the product at every stage of the processing include judicial selection of passive container materials and environments. Therefore, vacuum treatment and processes using containerless or crucibleless techniques are undoubtedly the most preferred and hence usable methods and nevertheless constitute an essential part of any purification scheme to achieve ultrapure refractory metals.

A. Pyrovacuum Treatment

Pyrovacuum treatment at elevated temperatures purifies significantly the refractory metals produced particularly by metallothermic reduction of their oxides and halides, as their thermits contain impurities like residual excess reactants, by-products and interstitial impurities that might have been picked up during the reduction process. Although vacuum treatment alone may not produce the degree of purity achievable by zone refining or other process, it offers a less expensive method for producing metals of adequate purity for several applications.

Purification in pyrovacuum treatment may take place by the following mechanisms: (a) evolution and removal of oxygen, nitrogen and hydrogen gases, (b) vaporisation of suboxides (sacrificial deoxidation), (c) carbon and oxygen reaction for removal of CO (decarbonisation), (d) vaporisation of volatiles (residual reactants, by-products or dissolved metals) and (e) flotation or settling of non-metallics.

Degassing of molten metals on evacuation is facilitated because the solubility of gaseous elements like O, N and H in the melt decreases when the partial pressure of these gases in the surrounding environment is lowered. The removal of gaseous impurities is governed by the well-known relationship $S_G = k P_G$, designated as Sievert's Law. According to this law, the concentration or solubility of a diatomic gas, S_G, is directly proportional to the square root of the partial gas pressure, P_G (k being the proportionality constant). The success of purification depends on experimental parameters such as ability of vacuum system to maintain low gas partial pressures on the melt surface, stirring action in the liquid phase and the composition of the starting material.

Purification by sacrificial deoxidation takes place by preferential evaporation of metal suboxides, i.e., removal of oxygen impurity. This occurs because the vapour pressure of the suboxide just above the melting point of the metal being refined is higher than that of metal vapour pressure. If one defines the degree of purification by sacrificial deoxidation, R, as the ratio of molar concentration of oxygen in the evaporating mixture to that in the molten metal, i.e., $R = (O/M)_{vap}/(O/M)_{melt}$, one obtains values of R for various refractory metals (thermodynamically) /3-6/; these values fall into two significant and separate groups: a first group of refractory metals having R values more than unity, i.e., the oxygen content in the melt decreases by volatilisation of the suboxide, and a second group of refractory metals with R values less than unity, i.e., these metals do not deoxidise. In practice, favourable purification by sacrificial deoxidation is expected if R becomes about 10. However, with R values of 10, about 10% of the metal would also be lost in reducing the concentration of oxygen to half of its value. Estimation of R values for several refractory metals was calculated by Sundaram et al. /4/ and these values are reproduced in Table 2. These values indicate that sacrificial deoxidation is suitable for metals like Nb, Ta, Hf and V. In the case of refractory metals, namely Mo and W, evaporation is via a series of oxides of these metals such as Mo_3O_9, MoO_3, MoO_2, W_3O_8, WO_3 and WO_2 /7/, and this facilitates purification. However, in the final stage (above m.p. of these metals), the residual oxygen is removed in the form of atomic oxygen.

Another mecnanism responsible for removal of the last traces of oxygen from metals is reaction of the oxygen with carbon to form carbon monoxide in accordance with the expression,

$$C_{(metal)} + O_{(metal)} \rightleftharpoons CO_{(gas)}$$

where $C_{(metal)}$ and $O_{(metal)}$, respectively, represent the solubility of carbon and oxygen in metal. Carbon deoxidation of groups IV, V and VI metals was described by Garg et al. /3/. From the established data, it is shown that groups Va and VIa metals tend to deoxidise (group Va metals more), the carbon deoxidation of group IVa metals is not possible on account of their large affinity for oxygen and low equilibrium partial pressure of the resulting CO gas, which is equivalent to the vapour pressures of metals themselves.

TABLE 2
R VALUES FOR REFRACTORY METAL - OXYGEN ALLOYS (REF. 3-6)

Metal	Temp. (K)	Vaporising species	Values of various compositions (in atom. % oxygen)					Limiting R values
			20	10	3	2	1	
Hf	2.500	HfD	4.0	6.0	9.0	12.0	13.0	15.0
V	2.200	VD	2.2	3.5	4.8	5.5	6.0	6.3
Nb	2.800	NbO	4.0	9.0	19	50	100	$1.6x10^4$
Ta	3.300	TaO	4.0	9.0	19	50	100	$3.0x10^3$

A good account of high temperature interactions of refractory metals not only with oxygen but also with N_2, H_2, C, CO, hydrocarbons and H_2O has been given by Schulze et al. /8/, in which various types of gas-metal reactions, the equilibria and thermodynamics for the solid solution range of the non-metal are discussed. Since refractory metals are mostly used in high temperature environments, kinetics and mechanisms of reactions with N_2, O_2, H_2O, CO and hydrocarbons are treated with emphasis in the high temperature regime. The purification by degassing of H, N, O and C (via H_2, N_2, MO_n, O_2 and CO) from solid or liquid metals by pyrovacuum treatments is only possible if the equilibrium pressure or vapour pressure of the desorbing species is higher than the respective partial pressure in the ambient gas atmosphere. The pressures depend on the non-metal concentrations in the metal and on the temperature. In Fig. 1, the final concentrations of H, N, O, and C+O in refractory metals established in H_2, N_2, O_2, H_2O and CO environments at 10^{-6} mbar are plotted logarithmically as a function of reciprocal temperature. At the high temperature of 2200 °C, the final concentrations (C_f values) between 10^{-2} and 10^{-8} at% of dissolved H,.N, O or C+O are reached in several refractory metals like Nb, Ta, Mo and W.

Mention may be made here of a unique solid state deoxygenation technique for purifying refractory metals which consists in annealing of the metal in presence of

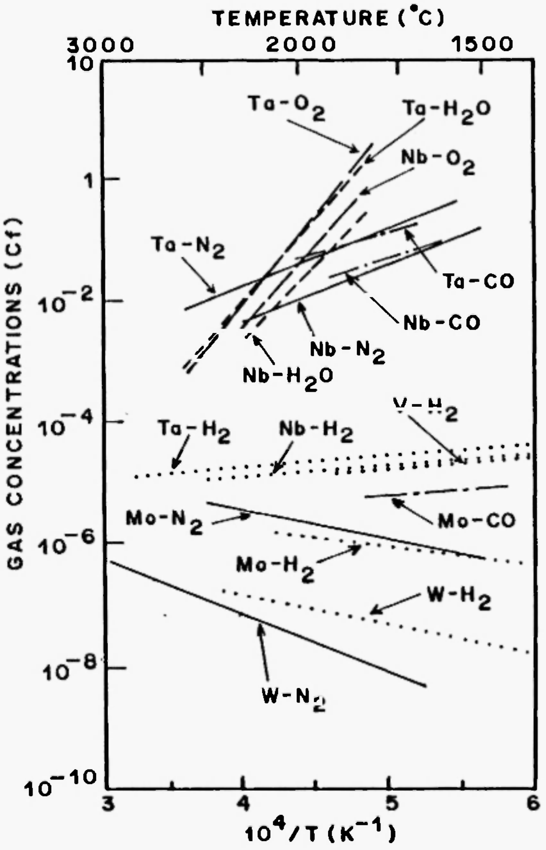

Fig. 1: Final concentrations of gases in refractory metals (after /8/).

another metal whose affinity for oxygen (or other interstitial impurities) is higher than the base metal. Successful application of this technique has been reported in vanadium metal /9,10/ for the removal of O, N and C by the use of getters Zr and Ti metals. Several of the refractory metals can be purified simultaneously and significantly by selective volatilisation of the impurities during the process of vacuum melting. The extent of purification achieved depends on the concentration of the impurity in the melt and in the vapour phase. For a binary system, the purification is governed by a relative volatility factor α, defined as $\gamma_a P_a^o / \gamma_b P_b^o$ where γ_a and γ_b are the activity coefficients and P_a^o and P_b^o are the vapour pressures respectively for the solute (impurity) and the solvent (base metal). The rate of removal of an impurity is not determined by the value of α only but also by the rate of transfer (diffusion) of the vapour from the surface of the melt to the condensing surface. Evaporation can be inhibited by the presence of a film covering the evaporating surface. Also due to evaporation of the more volatile constituent (an impurity), a concentration gradient will be set up in the melt and the diffusion rate of this constituent in the melt will then limit its evaporation rate. In practice, to effect purification by volatilisation, the vapour pressure of the impurity should be more than 10^{-3} torr (~mbar) at the working temperature, and it should exceed the vapour pressure of the base metal by a factor of at least 10.

Applications of pyrovacuum treatment to purify refractory metals are diverse and include treatment in molten or solid states. Treatment in the molten state may be required for refractory metals that are produced as thermits, electrolytic deposits, iodide deposits or as consolidated forms by powder metallurgy; it constitutes an inherent process during the zone refining. The pyrovacuum treatment of solids, restricted in general to removal of the trace interstitial impurities, may relate to processes like sintering, solid state deoxidation in presence of a getter, annealing or electrotransport.

Among the metallothermic reductions, the aluminothermic reduction of oxides followed by pyrovacuum melting of the metal thermit is an established method for the production of pure metals /11-15/ of groups Va and VIa. Table 3 shows the results of purification of the metals prepared by aluminothermic reduction of refractory metal oxides with subsequent volatilisation of impurities by vacuum heating.

In view of the high efficacy of vacuum melting in obtaining high purity products, it may be worth men-

TABLE 3
RESULTS OF PYROVACUUM TREATMENT TO PREPARE SPONGE FROM METAL OBTAINED BY ALUMINOTHERMIC REDUCTION (REF. 3)

Thermit	Thermit analysis (wt%)				Soaking temperature °C	Sponge analysis (wt%)			
	Al	Fe	Mn	O		Al	Fe	Mn	O
V	11.1	0.08	-	0.290	1700	1.42	0.035	-	0.010
Nb	2.0	0.11	-	1.500	1800	0.20	0.050	-	0.550
Ta	12.0	-	5	-	1950	1.00	-	0.3	-
Mo	4.9	0.50	-	0.085	2300	0.51	0.500	-	0.001

tioning here the various melting techniques which are prevalent for use for melting refractory metals. The high affinity of these metals for interstitial contaminants (O, H, N and C) necessitates all melting operations to be carried out either in vacuo or in an inert atmosphere. Secondly, contamination likely to be picked up during melting from the container materials or other sources such as heating devices or components should be kept minimal. Heating to melt by resistance has no place in the commercial production of refractory metals due to inefficient heat transfer from the source to the metal charge and also due to non-availability of passive container materials, i.e., those which have to withstand higher temperatures than the molten metal in question. Use of induction heating for melting is advantageous over heating by resistance because it permits melting operations at comparatively lower temperatures of the containment vessels. However, during induction melting, contamination by the container materials, which is more pronounced at lower pressures, cannot be ignored. These difficulties are circumvented in the case of vacuum melting by vacuum arc and electron beam meltings. In both of these methods, contamination from the container materials is eliminated by carrying out the meltings in water-cooled copper containers. Two main requirements for successful arc or electron beam melting, i.e., the metal must be shaped into a suitable electrode and the metal must possess low vapour pressure, are incidentally met by most of the refractory metals. However, refractory metals that cannot be formed into electrodes can be melted by the non-consumable electrode method. While the non-consumable electrode method can produce ingots of limited charge, the consumable electrode method can produce ingots weighing up to several tons of materials. As far as the purities that can be achieved are concerned, electron beam and arc meltings produce better purity than that obtained by induction melting. However, electron beam and arc meltings have their limitations, such as inability to raise metal temperature sufficiently to facilitate evaporation of impurities and the excessive degassing of the molten stage is shortlived.

In electron beam melting the charge is kept in a water-cooled copper hearth which is provided with a gun system comprising a cathode and anode and the whole system is evacuated to better than 10^{-4} torr. The electrons emanating from the cathode at high potential difference (10-40kV) hit the specimen which is melted. The main advantages that electron beam melting has over the arc melting are (i) longer time duration for the molten state, (ii) much lower pressures over the molten pool and (iii) possibility of considerable superheating the melt to facilitate some reactions which otherwise are slower to proceed just above the melting point. Perhaps the most spectacular use of electron beam melting in purifying refractory metals is in the form of electron beam floating zone melting (EBFZM) described later.

Another vacuum melting technique deserving mention with the above techniques is the levitation melting even though it is achieved through the application of induction melting. Contrary to other vacuum melting techniques, it can accommodate only a few grams of metal and, therefore, has limited use. By correct design of the induction coil, the specimen can be held suspended in vacuum, thus preventing contact with any container material. Among the refractory metals being included in this article, levitation melting of aluminothermic Nb metal /16/ has resulted in substantial removal of residual aluminium metal and other impurities present. Tungsten will lift but not melt and tantalum will not lift. The success in levitation of Nb, in fact, has become handy in carrying out the trace analysis of nitrogen in Nb by the high temperature vacuum fusion method.

B. Electrorefining

Due to their strong affinity for certain interstitial impurities, some of the refractory metals are not amenable to purification by application of the pyrovacuum treatment. Alternate processes such as fused salt electro-refining, iodide refining, zone refining, etc. are applied to achieve better purification.

Fused salt electrolysis has been successfully adopted to refine several refractory metals produced by metallothermic reduction /4,15/. Considerations for the choice of fused salt solvent are (i) m.p. of the salt should be convenient, (ii) salt should be thermally stable and should have low vapour pressure at the working temperatures, (iii) physiochemical properties of the salt, e.g.

conductivity, viscosity, surface tension, etc. should be suitable, (iv) salt cations should be more noble than the metal to be electrowon (electrochemical series of cations depends on the fused salts employed), (v) solubility of refractory metal compound in the salt should be high and, (vi) anode should be wettable by the fused salt and support an anodic reaction.

In electro-refining the impure metal is made the anode of the electrolytic cell which is dissolved electrolytically and redeposited as pure metal at the cathode. The overall electro-refining reaction can be written as

$$M_{impure} \longrightarrow M^{n+} + ne \quad \text{(at the anode, oxidation)}$$

$$M^{n+} + ne \longrightarrow M_{pure} \quad \text{(at the cathode, reduction)}$$

$$\overline{M_{impure} \longrightarrow M_{pure}}$$

From the thermodynamic considerations, the free energy change for the above reaction can be expressed as

$$\Delta G^\circ = -RT \ln \frac{(a_{m^{n+}})\ \text{cathode}}{(a_{m^{n+}})\ \text{anode}}$$

and the cell potential E°_{cell} can be obtained from the equation

$$E^\circ_{cell} = -\frac{\Delta G^\circ}{nF} = RT \ln \frac{(a_{m^{n+}})\ \text{cathode}}{(a_{m^{n+}})\ \text{anode}}$$

where parentheses refer to activities of the metal ions.

Since electro-refined metal, i.e., deposited at the cathode, is almost pure, the $(a_m{}^{n+})$ cathode value can be equal to unity, thus rendering the above equation to the form

$$E^\circ_{cell} = -\frac{RT}{nF} \ln(a_{m^{n+}})\text{anode}$$

As the anode material (crude metal) is also reasonably pure, the value of (E°_{cell}) approaches unity and therefore would be relatively small. Under this condition the cell operates at a very low voltage. Also the anodic oxidation liberates enough energy for the deposition of the metal at the cathode, making electro-refining an efficient process due to the requirement of a very small potential drop to run the process and making the whole operation economically attractive.

To facilitate achieving ultra-purification of metals by electrolysis, selectivity of various ionic species at the cathode deposition has to be maintained. The electrode potentials provide such selectivities in the deposition of metals. From the knowledge of electrode potentials (which depend on the electrolyte type used) of the impurities, these are broadly divided into two groups: the nobler (less electronegative) and baser (more electronegative) than the metal to be refined. While the impurities, termed as nobler, do not electrochemically dissolve and get concentrated in the anode, the baser ones are readily oxidised (dissolved) at the anode and remain in the electrolyte without passage of any current. With the build-up of these impurities in the electrolyte some transfer to the cathode deposit may take place by way of chemical equilibria between the electrolyte and the cathode. The impurities having deposition potential close to that of metal to be refined, tend to co-deposit at the cathode and this tendency could be reduced by keeping their activities different in the electrolyte. The interstitial impurities such as O, N and C, if present in the anode feed, remain unchanged and stay behind in the anode.

The electrode potentials (in a fused salt medium) indicate only the order in which metals can get deposited. The mechanism and the overvoltage for the continuous electrodeposition are more simple in nature. The overall efficiency of the process depends, inter alia, on the following kinetic factors:

(i) The reaction equilibrium between the anode material and the electrolyte,

(ii) the diffusion of the materials to the anode surface,

(iii) the solubility of impurities in the electrolyte,

(iv) the diffusion and electrotransport of materials through the electrolyte, and

(v) the reaction equilibrium between the electrolyte and the cathode.

Other parameters governing the efficient functioning of the cell pertains to design and materials of construction of the electrolytic assembly. These include provision to conduct the cell in inert atmosphere because of extreme reactivity of refractory metals towards certain gases, special shapes and sizes of both the electrodes and appropriate choice of electrolytes – functional and auxiliary electrolytes.

Refining by fused salt electrolysis can be applied to various intermediates or products, obtained during the course of a processing scheme. Successful refining of several refractory metals, obtained by metallothermic reduction, by fused salt electrolysis has been reported by Suri et al. /4,17/. Thermits such as of Nb, Ta, V and Mo containing appreciable amounts of metallic and interstitial impurities have been electrorefined to a fair degree of purification as shown in Table 4. Electrorefining has been of particular utilization to obtain pure V as it is difficult to refine by pyrovacuum treatment on account of its high volatility compared to that of its suboxide. Ultrapure V /18-20/ has been obtained by double fused salt electrolysis followed by EBFZM or electrotransport. Multistage electrolysis of $NbCl_5$ with subsequent EBFZM and high vacuum annealing has resulted in the highest purity metal /21/. Difficult removable W from Mo during purification has been successfully removed from Mo by the application of molten salt electrolysis /22/. Electrolytically deposited W using either WCl_6 or WO_3 feed material has facilitated preparation of W metal powders with minimal Mo content and having higher flow rates and better compressibility /23/.

C. Iodide Process

The iodide process essentially belongs to methods by which the purification is brought about by chemical vapour deposition and is one of the most extensively employed processes to obtain high purity Zr /24/, Hf /25,26/, V /30/ and Ti /27/; other refractory metals are also refinable by this process. This process is also known as the van Arkel-de Boer or the 'hot filament' method and was developed as early as 1925 /29/. The process is based on the reversibility of a reaction between the elementary metal and iodine (in principle, any suitable halide can be employed), which may be expressed as:

$$M_{crude} + nI_{2(g)} \xrightarrow[\text{low temp}]{T_1} MI_{2n(g)}$$

$$MI_{2n} \xrightarrow[\text{high temp}]{T_2} M_{pure} + nI_{2(g)}$$

The forward reaction takes place at a lower temperature T_1, while the reverse reaction, i.e., the

TABLE 4
RESULTS ON FUSED SALT ELECTROREFINING OF METALS FROM THERMITS (REF. 4)

Analysis in ppm	Vanadium		Niobium		Tantalum		Molybdenum	
	before	after	before	after	before	after	before	after
Al	47.700	100	20.000	20	47.300	<75	31.500	10
B	-	-	45	<5	45	<5	-	-
C	-	20	680	200	650	250	100	10
Fe	4.200	1.500	1.100	60	1.200	100	1.800	20
Mn	-	-	80	10	75	<10	-	-
N	768	30	320	100	400	100	200	20
O	8.000	900	15.000	1.000	550	200	1.000	50
Si	4.400	50	1.300	180	1.500	455	1.500	70

decomposition, takes place at a much higher temperature T_2 to yield pure metal and the iodine. The pure metal gets deposited on an incandescent filament (at T_2) made from a compatible metal, and the released iodide vapour is recycled, viz. it diffuses back and reacts with the crude metal forming fresh metal iodide.

Purification in this process takes place because of the following favourable conditions:

(i) Metal iodides are generally less stable than their corresponding bromides and chlorides,

(ii) the interstitial impurities such as O, N and C present in the crude metal do not react with iodine at the temperature T_1,

(iii) the m.p. of the metal is higher than the dissociation temperature of the iodide,

(iv) respective iodides of some impurities at T_1, if formed, do not decompose at T_2, and

(v) some impurities (present in elemental form) are too volatile at T_2 and do not remain in the hot filament zone even if their iodides are formed and decomposed along with the base metal.

The efficacy of the process depends on factors such as the type of metal, types and extent of impurities present in the crude metal, temperature T_1 for iodide formation, amounts of crude metal and the total elementary iodine in the beginning and the geometry of the vessel assembly.

Iodide refining has been successfully applied to several metals (Table 5). While the method is by and large applicable to refining of most of the refractory metals, metals such as Zr, Hf, V and Ti /4,25/ of purity better than 99.95% have been prepared as crystal bars in kg quantities.

D. Zone Refining

Zone refining was developed in the early 1950's by Pfann /31/ in response to the need for high pure semiconductor material germanium. By applying this technique, Pfann was able to decrease the impurities to a

TABLE 5
RESULTS OF IODIDE REFINING OF REFRACTORY METALS (REF. 4, 25)

		Impurities (ppm)							
		O	N	H	C	Al	Fe	Si	Mg
Hf	before	6900	250	-	-	-	580	-	-
	after	172	22	-	-	<30	110	-	-
V	before	600	1800	50	-	-	100	-	<300
	after	40	<5	10	150	-	30	20	150
Zr	before	1360	41	-	132	50	95	120	-
	after	230	29	-	115	10	<15	55	<10
Ti	before	4800	127	-	613	<50	220	665	300
	after	150	40	-	105	<50	75	195	50

level of one part in 10^{10} parts of germanium, i.e., 0.1 p.p.b. – a degree of purity not yet achieved by any known method. Rapid developments in the fields of electronics, nuclear and space sciences during the last few decades have created demands for a host of materials having extremely high purity. This in turn has resulted not only in wide applications of zone refining technique to achieve this goal but also in various modifications of the technique. Perhaps the most significant among these is the floating (crucible- or container-less) zone refining employed for the purification of refractory metals /32-37/.

The concept and theory of zone refining have been reviewed by others /31,38-42/. In this technique, the purification of a substance is dependent on the difference in solubility in the liquid and the solid phases of an impurity element (solute). The zone refining operation consists of creating a narrow molten zone in a relatively long solid ingot charge and then making it traverse through the whole length of the charge. As the molten zone (having two liquid/solid interfaces) moves, the impurities redistribute themselves at the crystallising liquid/solid interface in accordance with their solubilities' difference in the solid and liquid phases. The key parameter governing the degree of purity is the equilibrium distribution coefficient k_o, defined first by Pfann, with the aid of a binary phase diagram of a solute (soluble impurity) and a solvent (the host material) as the ratio of concentration of the solute in the crystallising solid C_s to that in the liquid C_l. An expression for a single molten zone pass operation showing the solute concentration in the solid state at a distance x from the starting end and a function of the initial uniform concentration C_o, the molten zone length l and the effective distribution coefficient k as derived by Pfann /31/ is $C_s/C_o = 1 - (1-k)^{-kx/1}$.

The effective distribution coefficient k is related to the equilibrium coefficient k_o according to Burton et al. /43/ by the equation:

$$k = k_o / \left[k_o - (1-k_o)e^{f\delta D}\right]$$

where f is the freezing velocity, δ is the thickness of the depleted or enriched solid/liquid interface and D is the solute diffusion coefficient in the liquid. The solute distribution after n passes has been derived by Reiss et al. /44/ for an infinite ingot length. Lord /45/ has also derived an expression for the solute concentration as a function of the distance in zone lengths from the starting end and the number of passes.

In a specific solvent-solute system, for a given number of molten zone length l and distance x, the degree of purification is basically dependent on the number of zone passes n and the effective distribution coefficient k, the latter parameter being a function of traverse rate of the zone. The slower traverse rate and larger n tend to enhance purification.

For low melting substances, the technique of zone refining can be conveniently applied as suitable and passive container materials are available to hold the charge and molten zones. However, for high melting substances, such as refractory metals, whose slightest contact with other materials at their m.ps poses contamination problems due to the extreme reactivity, the zone refining most successfully applied is termed as floating zone melting (FZM), i.e., molten zones do not come in contact with any container or crucible material.

The development of FZM was due to Keck and Golay /32/, Emeis /33/ and Theures /34/ for the preparation of electronic grade silicon. The technique was extended for obtaining high purity refractory metals /36,37,46,47/. The technique envisages holding of a molten zone in place between two vertical solid rods (compacted or otherwise) by its surface tension. The production of molten zone is accomplished mostly by induction or electron beam melting. The intactness or stabilisation of the floating molten zone length is a crucial exercise of the operation and depends upon surface tension and density of the molten metal.

Inductively heated specimen to produce a floating molten zone may be possible at any positive pressure of inert, reducing atmosphere or in vacuo. Other benefits arising out of the use of induction melting are the automatic electromagnetic stirring of the melt, increased stirring of the molten zone due to levitation forces and incorporation of better control of the zone diameter by sensing conductivity of the load /48/. The disadvantage with this type of heating, however, is the difficulty in generating high temperature in a narrow molten zone; a requirement for simultaneous refining of the refractory metals via volatilisation of impurities.

The electron beam floating zone melting (EBFZM), first demonstrated by Calverley et al. /49/, on the other hand, can produce a very narrow molten zone in refractory metal specimens by bombarding with electrons accelerated through a high voltage field. Also the control of the molten zone length is easier by manipulating the electron beam, though the whole operation warrants the use of vacuum better than 10^{-4} torr ($<1.33x10^{-2}$ Pa).

The technique of EBFZM has been reviewed by several authors /50-52/ and the main merits and demerits of the technique are listed below.

- Merits: Small melt volume, well-defined thermal gradients, no crucible contamination and efficient heating.
- Demerits: The use necessitates high vacuums (10^{-4} torr) and therefore high vapour pressure or dissociable materials cannot be processed. Fortunately this situation does not arise in the case of refractory metals which have low vapour pressures at their m.ps. (see Table 6).

FZM when performed in vacuo has additional benefits, i.e., apart from conventional zone refining taking place due to segregation of impurities, vacuum degassing, deoxidation, decarbonisation and selective volatilisation of impurities also occur simultaneously. For instance, it has been estimated by Schulze /21/ that segregation removal of impurities like Fe, Al, Cr and CO, enriched during prior electrorefining of Nb, constitutes only a minor part of the total purification effect on EBFZM of Nb. The major purification mechanisms that occur are volatilisation of metallic impurities, outgassing, decarbonisation and sacrificial deoxidation. The efficacy with which the interstitial impurities are removed from the refractory metals simply by EBM has been tabulated by Paul /25/ (see Table 7). The data in Table 7 indicate that just by making two electron beam meltings oxygen content in Hf has been reduced to 170 ppm from the original value of 1550 ppm in the starting material. In Nb, oxygen has been reduced to 21 ppm from 655 ppm, in Ta to 30 ppm from 8900 ppm, in V to 225 ppm from 1045 ppm, in Mo to 6 ppm from 810 ppm and in W to 5 ppm from the original value of 4100 ppm – the oxygen removal has been effected due to sacrificial deoxidation in these metals. However, as can be seen from Table 7, the removal of both carbon and nitrogen interstitials from these metals on EMB is comparatively lower.

Certain impurities having unfavorable volatilities may not get even segregated during EBFZM if the distribution coefficient values are near unity. This is precisely the case with the metallic impurities Ta and W present in Nb. These neither get volatilised nor do they

TABLE 6

EVAPORATION LOSS OF REFRACTORY METALS DURING VACUUM ZONE REFINING (REF. 25)

Metal	m.p. (°C)	Approximate vapour pressure (torr)	Evaporation loss in $mg/cm^2/minute$
Hf	2227	$4.0x10^{3}$	3.90
V	1890	$4.0x10^{-2}$	21.24
Nb	2468	$1.6x10^{-3}$	1.79
Ta	2996	$3.2x10^{-3}$	2.60
W	3410	$2.5x10^{-1}$	19.72

get removed by segregation because the values for k_{Ta} and k_w in Nb are respectively 1.4 to 1.7 and 1.7 to 2.0. Schulze /21/ has been able to effectively remove both Ta and W in Nb by double fused salt electrorefining prior subjecting to EBFZM for further purification. By combining EBFZM and ultra high vacuum annealing of the electrolytically deposited metal, Schulze was able to achieve a purity with less than 1 ppm of interstitial impurities in the final product. Removal of interstitial impurities from V employing EBFZM has been studied by Reed and Bressers /53,57/. Although in V the success by EBM is less pronounced than the other b.c.c. metals, the technique is adequately efficient to remove interstitials O, C and H. The removal of N in V has been studied at large by applying EBFZM but the results of the studies are rather confusing /55-57/. Removal of interstitial impurities O, C, N and H each less than 1 ppm in W and Mo by EBFZM has been reported by Glebovsky et al. /58/. Difficult removable metallic impurities for these metals, such as Si, Fe, No and Al, were also removed effectively on processing by EBFZM.

The results of metallic as well as interstitial impurities removed by the application of FZM in refractory metals Hf, V, Nb, Ta, Mo and W are supplied in Table 8. The determination of metallic impurities has been done by gas discharge mass spectrometry (GDMS), carbon by combustion and O, N and H by fusion methods. FZM can be profitably employed for the ultrahigh purification of a metal containing only a few ppm of impurities. In the case of the refractory metals, the application of FZM is restricted to preparation of small quantities required for very special applications like measurement of basic physical and chemical properties.

TABLE 7
DATA ON ELECTRON BEAM MELTING OF REFRACTORY METALS (REF. 25) AFTER TWO CYCLES OF OPERATION

Metal	Specimen	Analysis (ppm)			
		H	C	O	N
Hf	Starting material	-	-	1550	70
	After two meltings	-	-	170	25
V	Starting material	16	-	1045	210
	After two meltings	12	-	235	95
Nb	Starting material	3	280	655	1085
	After two meltings	1	55	21	45
Ta	Starting material	4	500	8900	100
	After two meltings	1	44	30	26
Mo	Starting material	2	170	810	51
	After two meltings	1	25	6	3
W	Starting material	1	70	4100	30
	After two meltings	1	30	5	2

TABLE 8
IMPURITY CONCENTRATIONS OF ZONE REFINED REFRACTORY METALS BY GDMS (REF. 158)
(IMPURITY CONCENTRATIONS IN PPM wt%)

Element	V	Nb	Ta	Mo	W
Ag	<0.002	<0.3	<0.004	<0.7	<0.12
Al	0.1	0.15	<0.05	0.03	<0.07
As	<0.05	<0.01	<0.002	<0.01	<0.005
Au	0.6	<0.03	<0.2	<0.02	<0.3
Bi	<0.02	<0.01	<0.04	<0.12	<0.02
Ca	0.1	0.02	<0.008	0.04	0.02
Cd	<0.03	<0.5	<0.007	<0.1	<0.025
Cl	0.1	0.3	0.01	0.4	0.2
Co	<0.15	<0.01	0.3	<0.06	0.1
Cr	<5	0.05	0.2	0.1	<0.001
Cu	<0.3	<0.01	0.02	<0.02	0.005
Fe	<20	0.12	0.3	12	0.01
Ga	20	<0.01	<0.003	<0.02	<0.01
Ge	<0.6	<0.01	<0.005	<0.02	<0.04
Hf	<0.03	<0.02	<0.4	<0.03	<0.04
In	<0.03	<0.07	<0.02	<1	<0.03
Ir	<0.06	<0.01	<0.2	<0.03	<0.15
K	0.4	<0.04	0.02	1	<0.02
Li	<0.02	<0.01	0.001	<0.02	<0.001
Mg	<0.25	<0.05	0.006	<0.25	0.15
Mn	<0.15	0.03	0.01	0.06	0.03
Mo	0.08	<0.7	0.2	-	<0.1
Na	<0.05	<0.03	0.015	<1	<0.01
Nb	0.8	--	25	1	<1

TABLE 8 (continued)

Element	V	Nb	Ta	Mo	W
Ni	12	0.15	1.5	0.1	<0.02
P	0.2	<30	<0.05	<0.03	<0.05
Pb	<0.003	<0.02	<0.08	<0.03	<0.25
Pd	15	<0.5	<0.4	<1	<0.25
Pt	<0.04	0.02	<0.2	<0.06	<0.5
Re	<0.5	<0.02	<0.002	<0.4	<1
Rh	<0.5	<0.06	<0.001	<0.1	<0.06
Ru	0.1	<0.4	0.02	<0.3	<0.2
S	<0.02	<0.07	<0.004	1	0.07
Sb	20	<0.04	<0.02	<0.2	<0.03
Si	<0.03	0.6	<0.002	0.08	0.3
Sn	<0.3	<0.3	--	<0.4	<0.02
Ta	6	50	0.01	2	5
Ti	--	<0.02	0.01	<1	<0.01
V	7	<0.8	1.2	<0.02	<0.01
W	<0.4	6.4	<0.004	20	--
Zn	<0.12	<0.02	<0.1	<0.02	<0.02
Zr	<1	<0.03	--	<0.04	0.2

The use of FZM technique has been extended to obtain single crystals of refractory metals Nb /37,59-61/, Ta /61/, Mo /58,60,61-65/ and W /37,58,60,65/.

E. Solid State Electrotransport Processing (SSEP)

Solid state electrotransport or electromigration is another technique useful particularly in the removal of interstitial impurities from the refractory metals and has met with unprecedented success. It consists in passing of a high direct current (at high current densities) through an ingot of metal at elevated temperature, thus imparting motion (due to enhanced diffusion rates at elevated temperatures) to the solute atoms which get transported to one end of the ingot. Purification by electrotransport is basically different from chemical separation processes in that the redistribution of an impurity takes place within one phase rather than by partitioning between two phases. Also electrotransport need not necessarily remove the impurities from the metal phase; these merely get displaced within the phase.

The successful electrotransport purification of refractory metals has been possible so far only on a restricted small scale, primarily because of the inherent slow nature of the process and requirements of large currents. It has been applied mostly to metals in which the interstitial impurities are held so tightly that even on EBM these are not effectively removed. In Th, for instance, C and N are so strongly bonded that on EBM, Th evaporates leaving metal behind enriched with C and N. Application of SSEP brought down N from 60 ppm to < 1 ppm, C from 40 to < 2 ppm and O from 120 to < 10 ppm.

In Nb /67/, the direction of motion of O and C has been reported to vary with temperature, i.e., towards cathode at low temperatures and towards anode at elevated temperatures. By and large, for the transition metals of 4th, 5th and 6th periods, the direction of interstitial migration varies with the position of the host metal in the periodic table of the elements. Transport occurs towards the anode in metals belonging to VI, VII and VIII groups.

Purification by electrotransport is based on diffusion rates of interstitial atoms which are appreciably high at elevated temperatures. The electrotransport of interstitial atoms under the influence of a d.c. potential can be expressed by the equation /66/:

$$\mu_i = \frac{D_i e}{kT}\left(Z_i - \frac{\delta e_i}{e}\right) \tag{1}$$

where μ_i is the electric mobility, D_i the diffusion coefficient, Z_i the valence and e_i is the friction coefficient of the interstitial atom and e is the electronic charge. The direction of the transport is determined by the sign of the effective valence Z^*, which refers to

$$\left(Z_i - \frac{\delta e_1}{e}\right)$$

A negative sign of Z^* indicates the electron friction force to dominate and migration to occur towards the anode and vice versa.

During electrotransport apart from the motion of the interstitial atoms due to the applied electric field, there would also be a concentration diffusion in the opposite direction and therefore the net flux J may be expressed as:

$$J = -D_i \frac{dC_i}{dx} - C_i \mu_i E \tag{2}$$

where the left term pertains to concentration diffusion in the opposite direction and the right term represents the flux of interstitial atom due to electrotransport; C_i being the concentration, E the electric field and x the distance along the ingot length.

Now if one starts the electrotransport experiment with a host metal ingot having a uniform cross section, a uniform initial interstitial atom concentration and constant temperature, the concentration profile changes with time and a steady state condition will be reached such that the flux owing to back diffusion will be equal to the electrotransport flux. Under these conditions, i.e., when J = O, Eq. 2 will assume the form

$$-D_i \frac{dC_i}{dx} = C_i \mu_i E \tag{3}$$

Carlson et al. /68,69/ have made use of Eq. 3 for calculating the concentration profile of an ingot under steady state, reached after electrotransport, and have arrived at an expression as

$$\ln \frac{C_x}{C_o} = \ln \frac{\mu_i E l}{D_i} - \frac{\mu_i E x}{D_i} \tag{4}$$

where C_o is the initial (uniform) concentration and C_x is the concentration of the interstitial atoms at a distance x along the length l of the purified ingot. From Eq. 4 one can observe that the purification is enhanced with increased length l, electric field E (current density) and $\frac{\mu_i}{D_i}$ ratios. However, though the ratio indicates purification, it is not the sole criterion and one also has to consider the time factor to assess the desired level of purity.

Regarding the electrotransport purification in refractory metals, in practice all interstitial impurities migrate to the same direction thus making the process a single-step operation. Because of the elevated temperatures at which the solid is kept and the long durations of the process, application of this technique even to moderately volatile metal causes loss by evaporation and failure by melting at the cross-sectional area which may have been reduced due to localised evaporation.

The apparatus to carry out electrotransport essentially comprises a vacuum chamber, a mechanism to hold the specimen ingot, provision for high d.c. supply and arrangement for adequate cooling of the electric leads. A related matter of concern during operation is the avoidance of contamination from the surroundings and the transport of impurities from the electrodes or from the cooler ends of the specimen. Contamination from the surroundings is minimised by operating under high vacuum while transport of impurities from cooler ends are reduced by the use of adaptors made of high purity tantalum. Variation in experimental parameters and modification of apparatus are basically dependent on the metal to be purified. For instance, an environment of an inert gas at a low partial pressure is recommended for metals with appreciable vapour pressure at the experimental temperature because of loss due to sublimation.

As mentioned earlier, application of electrotransport to refractory metals has been on a limited scale. Typically ingots have a diameter of 2.5 to 8.0 mm, a length of 60 to 160 mm and an operation time ranging from 70 to 240 h. The application of an electric field is is of the order of 0.2 V/cm and the current densities are 200 to 2000 A/cm^2. In several instances, ingots of impure metal were provided by cutting from a single crystal and then subjected to purification by electrotransport. In other cases, the long time processing at an elevated temperature results in extensive grain growth and development of single crystals up to 2 cm long during electrotransport.

Extreme reactivity of refractory metals with interstitial atoms renders removal of their traces extremely difficult by processes like fused salt electrolysis, iodide refining and EBFZM. In several refractory metals, such as Hf /69/, V /20,54/, Nb /70/, Mo /71/ and Ta /72/, the application of electrotransport has resulted in interstitial impurities at levels never achieved before. However, for achieving ultimate purification at very low levels, the starting material for electrotransport processing should have interstitial impurities removed or reduced by either iodide refining or EBM.

Since the diffusion rates of interstitial impurities are higher in melt than in the solid state, innovative combination of electromigration with zone melting processing has experimentally been demonstrated to enhance the purification in case of W /73/. Evidently the most important care that one has to take during such processing would be the avoidance of interaction of the melt with the supporting material.

For most ultrapurification schemes, no single process would be adequate, even on multistaging, to achieve the desired purity. It is imperative to use a combination of methods for the targetted purity. Pertinent to efforts for achieving ultrapurification is the necessary care against contamination which is provided by employing passive container materials or containerless processing (melting in particular), using protective ambients and handling the intermediates or products meticulously. The various schemes adapted to achieve ultrahigh purification of Hf, V, Nb, Ta, Mo and W are given later in the article.

SPECIFICS OF ULTRA HIGH PURITY PREPARATION

Availability of moderately pure refractory metals has been known for decades; there seems to be no point in mentioning their historical perspectives. Within the last two decades alone obtaining the ultrapure refractory metals has been made possible largely due to the advances made in vacuum melting techniques; it is imperative to scrupulously exclude air and other contaminants in the extraction and working of these metals. Of the three major vacuum melting techniques, mention of which was made in the earlier part of the article, i.e., induction, arc and electron beam meltings, induction in melting is more or less an extension of air melting practice at very low pressures. Arc melting used in vacuo or an inert atmosphere was developed to process refractory metals in order to protect them from the interstitial contaminants as well as to avoid contact with the container material by using a water-cooled copper mould. Arc melting was introduced by Kroll for melting Ti under an inert atmosphere and its use was extended later to include processing of large quantities of other refractory metals Nb, Zr, Mo and W which warrant same type of melting conditions. Electron beam melting (EBM) is a rather more recent development of the three melting techniques. Combining EBM with floating zone melting, i.e., electron beam floating zone melting (EBFZM), introduced for ultra purification of refractory materials and the solid state electrotransport processing have yielded ultra high purity refractory metals which revealed some startling, unexpected and often, more useful properties.

It is appropriate to briefly give here a metal-by-metal account of the most satisfactory metallurgical processing scheme to obtain the refractory metals in pure form, including wherever possible the assessed purity (generalised) of intermediates or products obtained during the scheme.

A. Hafnium

Hafnium is the only refractory metal belonging to group IVa of the periodic table which is being included in the present article.

Hafnium always occurs in association with zirconium minerals because they both have the same charge and nearly identical ionic radii. Because of similarity in chemical and physical properties, Hf was mistaken for Zr for a long time. Because of the presence of variable amounts of Hf, even the atomic weight of Zr remained in doubt until 1923 when Hf was identified as a separate chemical element by x-ray spectroscopy and synthesised subsequently. In 1924 the first sizeable quantities of the two metals were obtained by van Arkel and de-Boer whose process, known as 'iodide method' /29/, continues to be one of the most accepted modern processes to obtain high purity metals like Ti, Zr and Hf.

The specific applications of the two metals are in the nuclear field; but ironically their use is based on their markedly different nuclear characteristics. While the use of Hf as control rod material is based on its high neutron (thermal) cross section (115 barn), Zr is used in the nuclear industry for fabrication of special alloys basically because of its low neutron cross section (0.18 barn). Non-nuclear application of hafnium are in the fabrication of getters, filaments, electrodes for x-ray generator, rectifier tubes and superalloys.

Zircon, $ZrSiO_4$, is the only Hf-containing mineral of commercial significance; Hf content varies from 1 to 5% as replcement of Zr.

Hafnium is always a by-product of zirconium extraction, available either in HfO_2 or $HfCl_4$ form. Winning of hafnium metal from $HfCl_4$ is preferred over that from HfO_2 and the general routes comprise both pyrometallurgical /77-82/ and electrometallurgical processing /83-85/, although several metallothermic reductions /86,87/ of HfO_2 have also been studied. Sharma et al. /87/ have studied the calciothermic reduction of HfO_2 with subsequent refining by vacuum sintering, electron beam melting, iodide method /25,27,87/ and fused salt electrolysis. The studies indicated that calciothermic reduction with subsequent iodide refining /25/ had resulted in good hafnium recovery of about 99.95% purity.

So far as the obtaining of high purity hafnium metal is concerned, three different routes are followed starting in each case with Hf sponge produced through Kroll process, i.e., reduction of $HfCl_4$ with Mg and pyrovacuum treatment to remove Mg and $MgCl_2$. The flow sheet to obtain high purity hafnium metal is given in Fig. 2.

Highest value for resistance ratio of purified hafnium metal as obtained from the open literature is 5,000 (Table 1 /74/).

B. Vanadium

Commercial grade vanadium oxide V_2O_5 is the main source of production vanadium metal. It is a by-product of processing different ores and minerals – Patronite V_2S, nS, Sulvanite $2CuS.V_2S_5$, Coulsonite FeO $(FeV)_2O_3$, Titanomagnetite $FeTi(FeTiV)_2O_3$, Carnotite $K_2O.2U_2O_3.V_2O_5.3H_2O$, Vanadite $Pb_4(PbCl)(VO_4)_3$ and Rosoelite $H_8K_2(Mg,Fe)(Al,V)_4(SiO_3)_2$. Vanadium is also recovered from the Bayer liquor left after aluminium extraction from bauxite, an important aluminium ore.

Crude vanadium oxide (black, 85%) obtained from ore concentrates is purified by precipitation as ammonium metavanadate NH_4VO_3, which is calcined to produce commercial grade V_2O_5 of 99% purity.

The major use of vanadium metal is as an additive to steels for hardenability or grain refining or as a carbide stabilizer in some high strength low-alloy steels. High purity vanadium is used in research and in alloy development work relevant to advanced reactor systems of both fission and fusion types.

Reduction of V_2O_5 to the metal is carried out either by calcium metal /89,90/ (older method), carbothermically /91/ or aluminothermically /11,14/. In the last method reduction is facilitated by an addition of 5 to 30% excess of aluminium over the stoichiometric amount of V_2O_5; the excess of aluminium also results in better separation of slag from the regulus. Although the product contains 5 to 30 wt% of aluminium, removal of aluminium does not pose a problem as the application of vacuum distillation /92/ (pyrovacuum treatment) facilitates its removal to yield a metal which is 99.8 to 99.9% pure. Electron beam melting /93,94/ or fused salt electrolysis /11,84,85,96/ or iodide refining /25,30,97,99,100/ of the crude metal raises the purity level substantially to about 99.95% (total metal content). Effective removal mainly of interstitial impurities O, N, H and C to improve purity has been demonstrated by employing electron beam floating zone melting /19,53,57,98/ solid state electrotransport /20,54,79/ and solid state deoxidation or decarbonisation /9,10/.

It may be worth noting here that by two-stage fused salt electrolysis, Lei et al. /18/ were able to get vanadium metal which was 99.95% pure (total metallic and interstitial impurities, less than 150 ppm). For ultrahigh purity vanadium the best RR values, i.e. 1000 to 2000, were obtained on material obtained by EBFZM

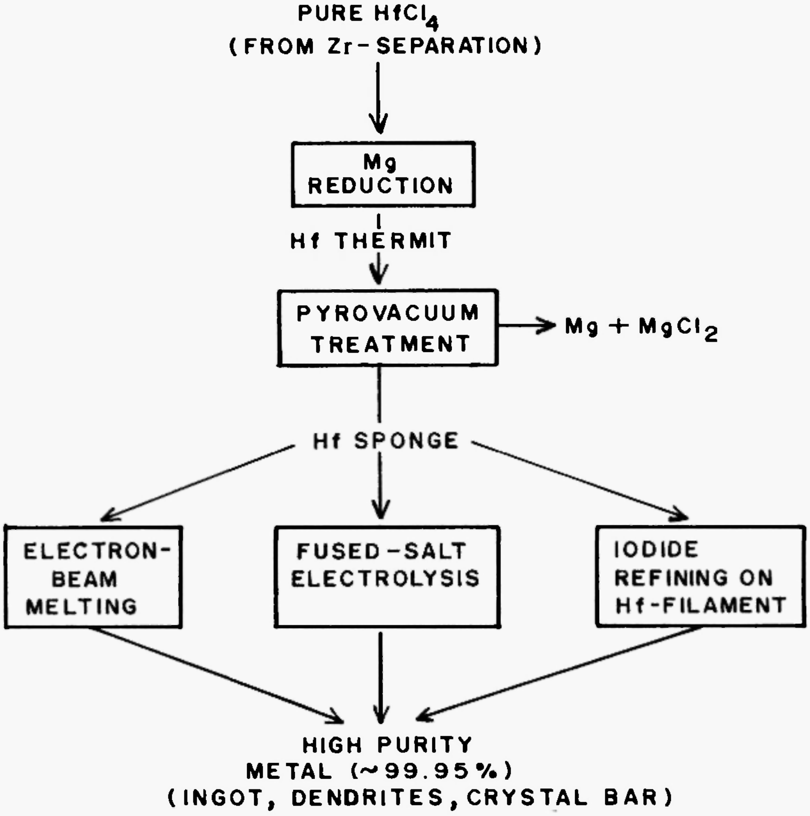

Fig. 2: Flow sheet to prepare high purity hafnium.

by Bressers et al. /19/. Carson et al. /20/ could remove the trace interstitial impurities by applying electromigration processing and obtained ultrahigh purity vanadium metal having RR value greater than 1880, total metallic purity of 99.999% and the interstitial impurity content less than 5 ppm (C < 2, O < 1, N < 0.5 and H < 1 ppm).

Attempts made by Peterson et al. /10/ for interstitial impurities removal by titanium metal gettering have shown very promising results in the reduction of N from 100 ppm to 1 ppm, C from 240 to < 2 ppm and O from 290 to 6 ppm.

A flow sheet to obtain ultrahigh purity vanadium metal is shown in Fig. 3.

Impurity concentrations of ultrahigh purity vanadium metal produced by zone refining, as estimated by gas discharge mass spectroscopy (GDMS), are shown in Table 8 /158/.

C. Niobium

Niobium and tantalum coexist in minerals because of their geochemical coherence and the two elements must be separated before reduction to metallic form.

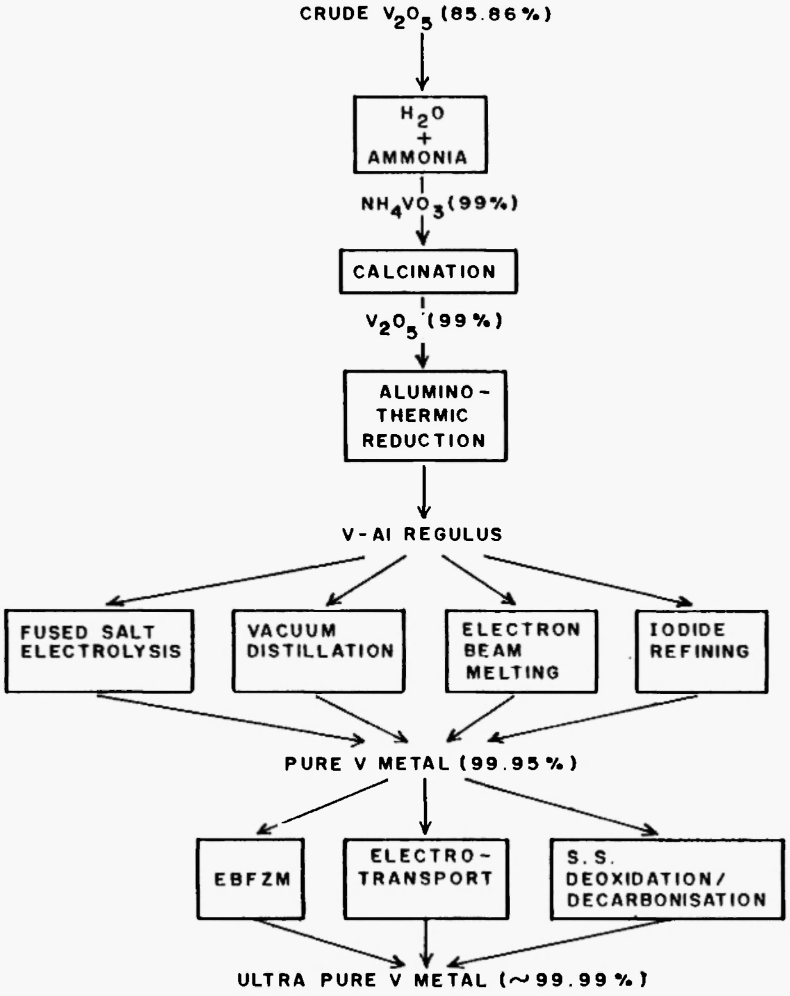

Fig. 3: Flow sheet for H.P. vanadium metal (purity in parentheses is generalised purity)

Separation processes are liquid-liquid extraction, fractional crystallisation of double fluorides of potassium and fractional distillation of the chlorides.

The occurrence of niobium and tantalum in mineral series pyrochlore-microlite and columbite-tantalite can be in a ratio that is indefinitely variable because of their isomorphic nature. Niobium is principally extracted from the mineral pyrochlore $(Na,Ca,Ce)_2 (Nb,Ti,Ta)_2 (O,OH,F)_7$ and its analogue pandaite – both high in niobium; niobium to tantalum ratio is 200:1 or more.

Due to the high cost of extraction and purification of niobium, it has very special applications which stem from its unique properties which are absent in less expensive metals. For instance, its high strength at elevated temperatures is utilised in fabricating advanced components in aerospace hardware, its low thermal neutron cross section (1.1 barn) and resistance to corrosion in liquid lithium and sodium metals makes it a candidate for nuclear reactor and fabrication of sodium vapour lamp applications and its super conductive alloy (Nb 46.5 Ti) has perhaps the single most important application as superconducting magnets. Ultrahigh purity niobium /21/ having a few at ppm of metallic and 1 to 2 at ppm of interstitial impurities is required for solid state studies such as radiation induced defects in b.c.c. metals, high energy neutron monitoring in reactor surveillance programmes, superconductivity, recrystallisation, surface properties, capacitor grade materials, etc. A recent use for ultrahigh purity Nb is for accelerating cavities in particle accelerators.

The breaking /102/ of niobium-tantalum mineral concentrates is effected by either alkali fusion, fluoride dissolution, chlorination or hydrofluorination. The separation of niobium from tantalum /101,103/ involves processes, fractional crystallisation of K_2NbF_7 and K_2TaF_7, liquid-liquid extraction using 50% tributyl phosphate (TBP) in kerosene or fractional distillation of their pentachlorides ($NbCl_5$ and $TaCl_5$). Depending on the separated niobium compounds, viz. Nb_2O_5, K_2NbF_7 or $NbCl_5$, the reduction route is chosen. Between Nb_2O_5 and K_2NbT_7, the former is more viable economically for reduction to produce niobium metal. The principal process until recently was carbothermic reduction of Nb_2O_5 (employing a mixture of Nb_2O_5 and NbC which has been superseded by the aluminothermic reduction process /3,12, 102,104,106-108/. This is due to several advantages favouring the latter process such as availability of cheaper and purer reductant aluminium metal, self-sustaining reaction and capability to carry out reduction in open reactors /106/.

Other reductive methods to produce niobium metal are sodium reduction of K_2NbT_7 with subsequent leaching /103/, fused-salt electrolysis of K_2NbT_7 /17,21,109-111/ with supporting electrolyte KF + KCl, and magnesium reduction of $NbCl_5$ /105/.

Consolidation of reduced metal powder in niobium ingots is accomplished by electron beam melting after appropriately removing impurities such as residual reductants (Al, Mg), products (Al_2O_3 slag, $MgCl_2$, NaCl etc.) and interstitial impurities (O, C, CO) by pyrovacuum treatments. For further purification of niobium metal, floating zone melting (FZM) /21,59, 112-114/ has been shown to be the most effective technique. For most of the floating zone meltings, electron beam melting is the preferred means of sustaining a narrow molten zone, but some attempts to employ radio frequency melting have also been reported /116/. Major purification during FZM occurs due to outgassing, volatilisation, gas-metal reactions (sacrificial deoxidation) and decarbonisation. Purification due to conventional segregation of impurities (arising on account of favourable distribution coefficients) on zone melting also takes place but to a lesser degree. In the case of niobium metal, however, the distribution coefficient /21,114/ for impurities Ta and W has values of 1.17 to 1.14 and 1.4 to 2.0, respectively, and these impurities pose difficulty in their removal on FZM. Another factor pertaining to EBFZM is the design of the electron beam gun, especially while considering W impurity removal from niobium metal. If an electron emitter for the gun made of conventional tungsten metal is employed for EBFZM of niobium, the W content increased (from the original 0.02 ppm to 2.9 ppm as reported by Schulze /21/) on zoning. This contamination from the electron emitter material was circumvented by the use of an electron emitter made of niobium itself.

Since the EBFZM of niobium is ineffective for the removal of impurities like Ta and W due to their unfavourable distribution coefficients, Schulze /21/ employed a scheme by which both these impurities are reduced below 1 ppm by double fused salt electrolysis prior subjecting to EBFZM. Final purification to remove trace interstitial impurities was accomplished by him through the use of ultrahigh vacuum annealing and a purity of 99.9995% was claimed, see Table 9. For comparing the analytical results given in Table 9 with those obtained on zone refined niobium metal given in Table 8, the role played by the fused salt electrolysis particularly in the removal of Ta and W impurities becomes apparent.

Another recent containerless technique developed for niobium processing is the levitation melting /115/. This technique has proved extremely useful for purifying niobium thermit obtained via aluminothermic reduction and electron beam melting. After subjection to the levitation melting, the product was about 99.96% pure.

As far as the measurements of resistance ratio of high purity niobium metal is concerned, Schulze /21/ made a brief year by year survey of the efforts directed towards preparing pure niobium and its purity assessment by RR measurement since 1965. Since high RR value does not necessarily mean low metallic impurity concentrations, Schulze's optimised method to produce ultrahigh purity niobium metal, whose impurity levels (see Table 9 for metallic concentrations and interstitials, C, N, O totalling to less than 1 ppm) were accurately determined by improved analytical techniques and RR values obtained were more than 104 (between 14,400 to 16,800).

Fig. 4 shows the various alternatives to obtain high purity niobium metal.

TABLE 9

CHEMICAL ANALYSIS BY PROTON/NEUTRON ACTIVATION ANALYSIS OF ULTRAHIGH PURITY NIOBIUM PREPARED BY ELECTROLYTIC AND EBFZM ROUTE (REF. 21)

Impurity element	In atomic fraction
Ta	0.05 - 3 ppm
W	1 - 50 ppb
Mo	75 ppb
Cr	17 - 44 pt
Fe	3 - 11 ppb
Co	6.3 - 30 ppt
Cu	<20 ppb
V	0.3 ppb
Ti	<0.1 ppm
Al	20 ppb

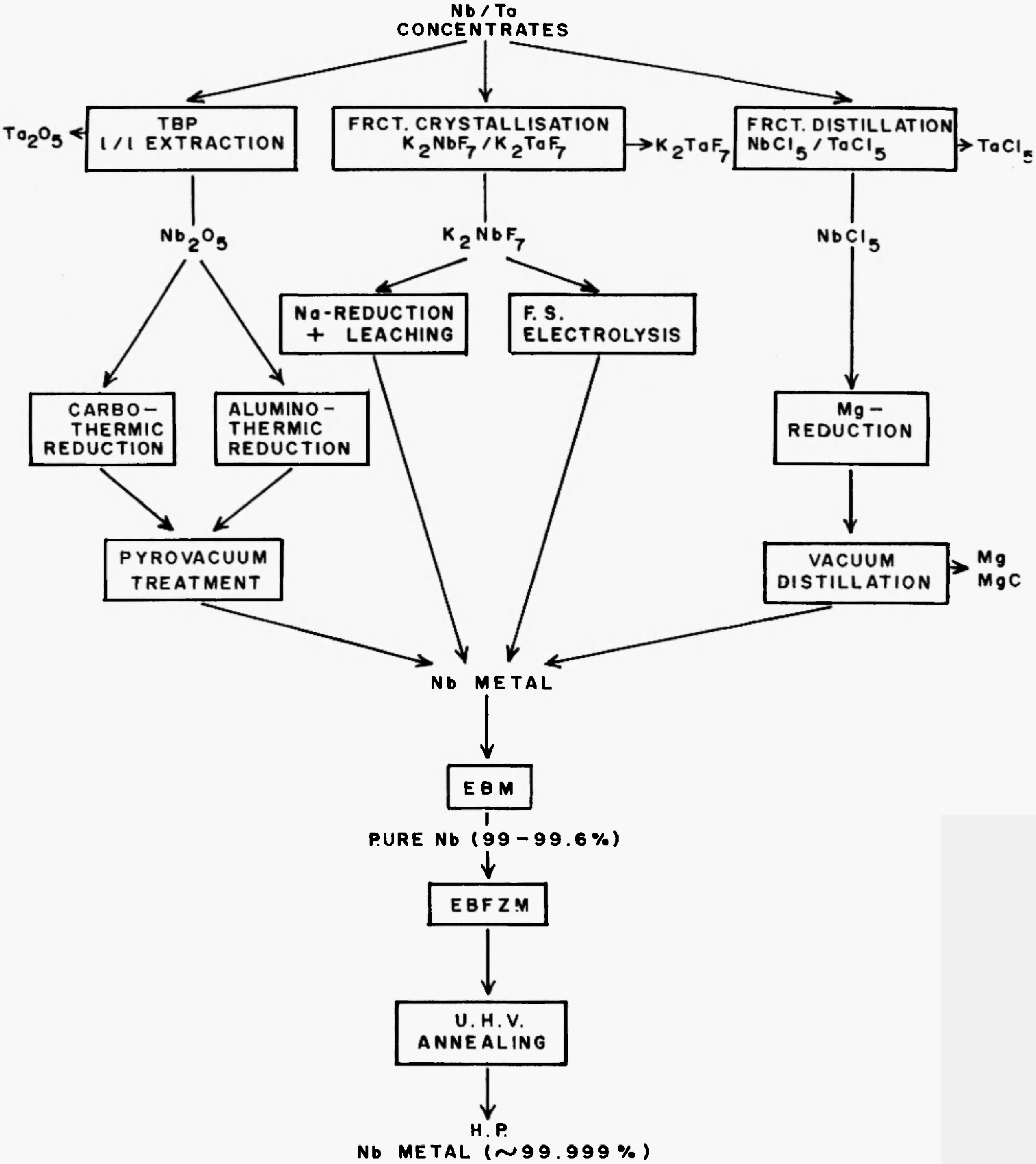

Fig. 4: Flow sheet for preparing high purity niobium metal.

D. Tantalum

Despite of its high m.p. (2994 °C), tantalum has excellent properties such as workability and low ductile-to-brittle transition temperature which render it workable at lower temperatures than other refractory metals. The major use of tantalum is in the fabrication of highly efficient and reliable electrolytic capacitors; a surface oxide film imparts to tantalum unusual rectifying and capacitance properties. Its very high resistance towards acids (except HF and fuming H_2SO_4) makes it a very compatible material for fabricating chemical processing equipment. Recently ultrahigh purity tantalum is being used in the fabrication of very large scale integration applications in which tantalum silicide $TaSi_2$ is implanted in various MOS device and circuits /1,2/.

Tantalum occurs in association with niobium in varying Ta to Nb ratios. Most of the tantalum metal is produced from tantalite, a ferro-manganese tantalite niobate (Fe, Mn)O(Nb, $Ta)_2O_3$, often found in low concentrations in pegmatites. The tantalite, having a Ta_2O_5 content up to about 85%, is concentrated before its conversion to a halide or oxide. High purity tantalum compounds of commercial importance, obtained after separation from niobium through liquid-liquid extraction or fractional crystallisation /103,107/ of the double flourides are, respectively, K_2TaF_7 or Ta_2O_5. These compounds are the starting materials for tantalum metal production or for conversion into carbides, other ceramics or additions for glass melts.

Reduction of Ta_2O_5 through carbothermic or aluminothermic route /107,118,119/ with subsequent pyrovacuum treatment to remove excess of the reductants /120/ and other impurities normally yields a metal which is about 99.5% pure.

Reduction with sodium metal /121/ or fused-salt electrolysis /17,119/ of K_2TaF_7 produces tantalum metal having a purity, by and large, slightly better (99.7%) than that achieved by route comprising metallothermic reduction and pyrovacuum treatment. However, recently Mimura et al. /125/ have demonstrated production of high purity tantalum metal (~99.97%) by carbon-reduction smelting of Ta_2O_5 using a plasma arc followed by hydrogen plasma arc melting. Enhanced tantalum purity (~99.995%) has also been claimed by metal reduction of K_2TaF_7, Albrecht et al. /103/.

Compacts of metal powders, obtained by any of the above mentioned ways, are sintered and electron beam melted /25,119,158/ to give a tantalum metal with total metallic purity of over 99.995%. However, further removal of interstitial impurities, O, C, N in particular, is accomplished by electron beam floating zone melting (EBFZM) /25,49,61,122/. Passage of a single molten zone /25/ causes a notable reduction in the interstitial impurities, i.e., initial concentrations of 100 ppm, 30 ppm and 35 ppm of O, C and N were respectively reduced by zone melting to < 30 ppm, 10 ppm and < 10 ppm. Electrotransport studies /25,70/ on the removal of interstitial impurities have shown these impurities to be transported to the cathode end of the specimen rod.

The resistance ratio, measured on high purity tantalum specimens obtained by combining zone refining and high vacuum annealing, is enhanced interestingly by as much as one order of magnitude when compared to the RR value measured without annealing. For instance, an RR value of 720 /123/ has been reported for zone refined tantalum metal while the RR value measured on an annealed tantalum sample was 7,000 /124/. Funk et al. /61/ have also recently reported an RR value of 7,000 for tantalum single crystal, grown by EBFZM, containing a total of interstitial impurities (O, N and C) less than 3 at ppm and tungsten impurity of about 10 at ppm, the latter being determined by proton activation analysis. The authors /61/ claimed trace removal of hydrogen in their tantalum specimen by coating the specimen with palladium metal and that of trace carbon by heating in partial pressure of oxygen; residual oxygen was removed by subsequent ultrahigh vacuum treatment.

A comprehensive analysis of the metallic impurities in zone refined tantalum metal by one of the latest analytical techniques, i.e., gas discharge mass spectrometry (GDMS), is shown in Table 8. A generalised flow sheet to obtain high purity tantalum metal is shown in Fig. 5.

E. Molybdenum

Molybdenum metal is seldom used as a base metal in alloy making. It is used mostly as an alloy addition

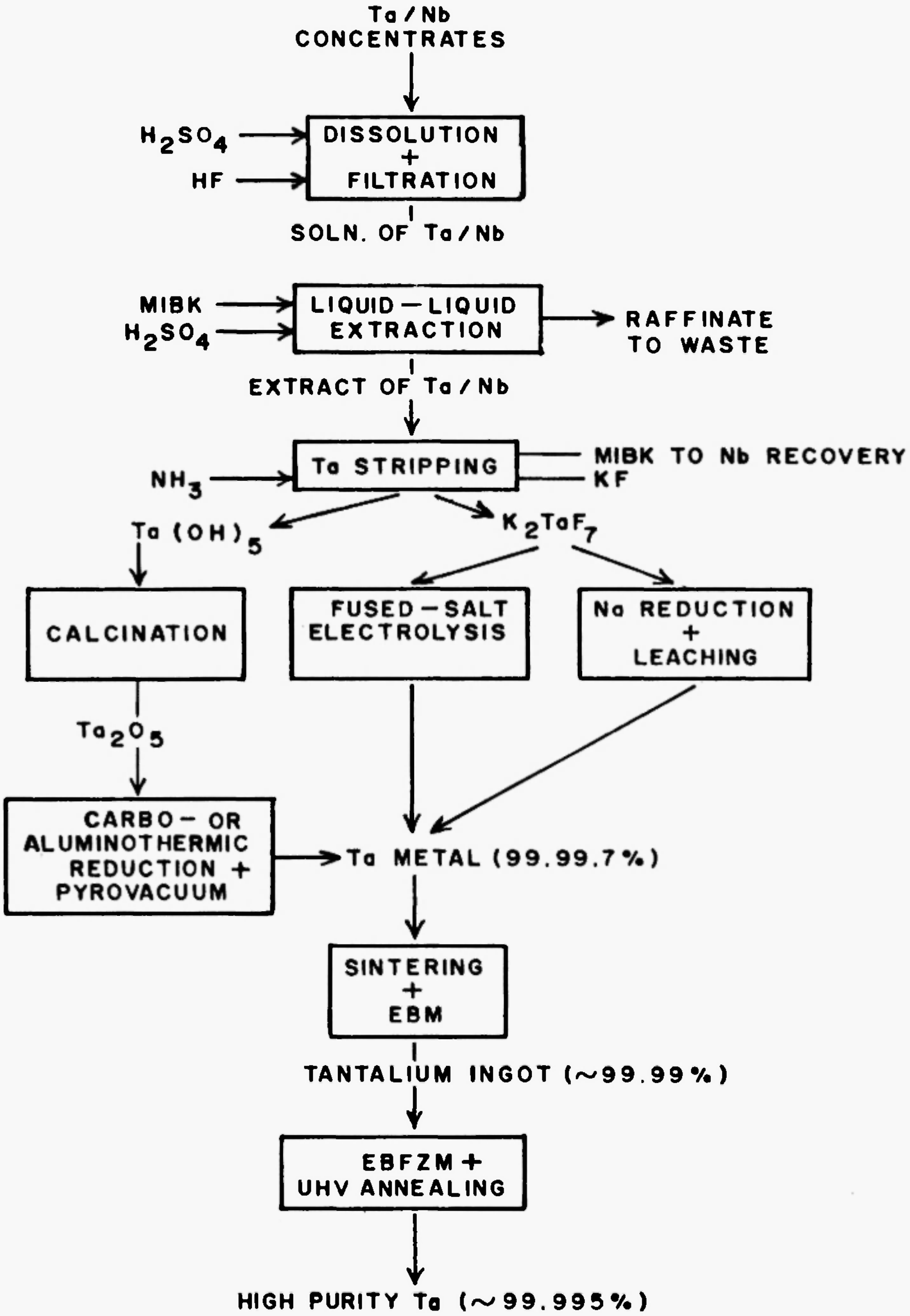

Fig. 5: Flow sheet to obtain high purity tantalum metal.

to irons, steels and some non-ferrous metals to enhance resistance to corrosion. Other uses of molybdenum and its compounds include catalysts, pigments, corrosion inhibitors, lubricants and smoke retardants. Recently, ultrahigh purity molybdenum /1,2/ has found use in very large scale integration applications.

The most important mineral of molybdenum is molybdenite MoS_2 and is the only one that is commercially used to obtain usable products such as ferromolybdenum (60Mo-40Fe) lubricant grade MoO_2 (~98%), pure molybdic oxide MoO_3 (~99%), pure ammonium dimolybdate $(NH_4)_2Mo_2O_7$ (~99%) and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ (~99%). Other Mo bearing minerals include powellite Ca $(Mo_2W)O_4$ and wulfenite $PbMoO_4$.

The molybdenite concentrates (97-99% MoS_2) are converted to high purity oxide MoO_3 either by roasting in air with subsequent subliming or through leaching, crystallising out ammonium hepamolybdate and calcining at 580 °C. Molybdenum metal is produced by hydrogen reduction of MoO_3 which takes place in a column or fluidised-bed reactor /126/ in two steps, i.e. $MoO_3+H_2 \rightarrow MoO_2+H_2O$ and $MoO_2+2H_2 \rightarrow Mo+H_2O$. Reduction of MoO_3 by hydrogen can also be effected to a single step operation at 900 °C /127/, provided hydrogen is preheated at 600 °C. Aluminothermic reduction of MoO_3 followed by pyrovacuum treatment to remove Al and O by sacrificial deoxidation was reported by Gupta et al. /128/. They obtained metal ingot on electron beam melting having impurity contents as 0.18% Al, 0.049% C, 0.015% N and 0.09% O. Mehra et al. /144/ have described a process by which calcium tungstate is aluminothermically reduced to give a yield up to 98.5%.

Of the metallothermic reduction processes to obtain molybdenite MoS_2, aluminothermic reduction /129-134/ has been found to be a preferred one because of its amenability to produce on large scale and the economics of the process. Subsequent pyrovacuum melting of the thermit or its fused-salt electrolysis yield molybdenum metal of purity varying between 99.55 to 99.9%. Electrorefining studies /17,133,135-138/ to obtain a better degree of purity have been carried out starting with molybdenum compounds such as Mo_2C /17/, Mo_2S_3 /17/ or MoS_2 /138/ since the use of MoO_3 as an anode is unsuitable due to its high volatility at the fused-salt electrolytic temperature. The use of Mo_2C with K_3MoCl_6 /17/ for electrolysis has resulted in cathode-deposited molybdenum, metal of ~99.95% purity (Al 10, Fe 20, O 50, N 20 and C 10 ppm). However, it should be noted that the majority of electrorefining studies have been directed towards obtaining molybdenum coatings or linings /135,136/ on certain substrate materials.

The application of powder metallurgy, vacuum arc melting and electron beam melting techniques have greatly facilitated consolidation of molybdenum powder into ingots which are further refinable by EBFZM /17,25,63,139-143/. Through EBFZM major impurities like Mg, Ca, Mn, Ni, Zr and Rh are removed by volatilisation; two exceptions, however, are W and C, especially when present in trace amounts. While the carbon content can be lowered to about 4 at ppm by subsequent annealing at 1600 °C in oxygen partial pressure followed by heating at 1800-2000 °C at $< 10^{-5}$ torr to remove residual oxygen gas, the removal of W traces could be effected by double fused-salt electrolysis prior to floating zone melting. Opperman et al. /22/ have shown an RR measured value of 6,35,700 for double electrorefined molybdenum metal having 1 ppm of W. Another RR value of ~70,000 has been assigned by Drangel et al. /140/ to a molybdenum ingot which had five cycles of EBFZM. They were studying the effect of several experimental parameters on the purity of resulting metal.

Electrotransport of molybdenum metal has been studied by Schmidt et al. /71/ who reported the interstitial impurities C, N and O to be positively charged and moved towards the cathode side of the specimen rod.

Growth of single of molybdenum metal has been reported by Glebovsky et al. /142/ who also included a comprehensive chemical analysis by SSMS of total metallic and interstitial impurities present in the crystal (see Table 10). The measured RR value on the crystal was 30,000. Another noteworthy high value for RR, i.e., 300,000 has been reported by Kimura /75/.

Because of the use of ultrahigh purity molybdenum and its silicide /2/ in the fabrication of very large scale integrated circuits in which the α-emitter impurities such as Th and U should be less than a few ppb, neutron

TABLE 10

ANALYSIS OF HIGH PURITY MOLYBDENUM METAL (SINGLE CRYSTAL); OXYGEN CONTENT BY FAST NEUTRON ACTIVATION ANALYSIS (FNAA) AND REST BY SPARK SOURCE MASS SPECTROMETRY (SSMS)

(AFTER REF. 142)

Impurity element	In atomic fraction
O	<0.5
C	<0.5
N	<0.6
H	<1
Si	<0.3
Al	<0.1
K	<0.1
Ca	<0.1
Na	<0.1
P	<0.03
S	<0.1
Mn	<0.03
Nb	<0.3
Ta	<0.1
Re	<0.1
V	<0.03
Fe	<0.3
Ni	<0.03
Co	<0.3
Cr	<0.03
Cu	<0.03
Pb	<0.1

activation analysis of the ultrahigh purity molybdenum has been described by Theimer et al. /145/. The results obtained by radiochemical separation of neutron activation analysis (INAA) of molybdenum metal are shown in Table 10. It is interesting to note that detection limits of less than 0.037 ng/g and 4.0 ng/g were reached by NAA for impurities Th and U, respectively.

Results of impurity concentrations in zone refined molybdenum metal as obtained by one of the recent mass spectrometric techniques, viz. gas discharge mass spectrometry (GDMS), are shown in Table 8 for comparison with the analytical data given in Table 10. Flow sheet to prepare high purity molybdenum metal is shown in Fig. 6.

F. Tungsten

Two basic reasons responsible for the relatively late discovery of tungsten are the difficulty in reaction of the metal from its minerals and the non-availability of suitable technology to consolidate and fabricate metals like W in the early metal industry. However, after its isolation and recognition of its unique properties in the mid 1800s, tungsten found applications in a wide range of alloys, compounds and as pure metal. The major areas of applications are filaments in electric lamp, heating elements, its addition for high speed and other tools, tungsten carbide tools and war-resistant parts and relatively recent ones being in space vehicles and nuclear reactors.

The two minerals of commercial significance are wolframite $(Fe,Mn)WO_4$ and scheelite $CaWO_4$. Tungsten ores are especially amenable to gravity separation because of high specific gravities.

Due to its extremely high m.p. (3410 °C) extraction of tungsten is done by hydrometallurgical processes /23,146/. The majority of the mineral concentrates are converted into high purity ammonium paratunstage $5(NH_4)_2O.12WO_3.5H_2O$(APT). Various extractive schemes are available to recover tungsten first as sodium tungstate Na_2WO_4. These include (i) caustic soda digestion of wolframite to obtain Na_2WO_4 which is purified by recrystallisation, (ii) hydrochloric acid leaching of scheelite to obtain H_2WO_4 slurry which on caustic digestion gives Na_2WO_4 solution and (iii) wolframite or scheelite is roasted with sodium carbonate and on leaching Na_2WO_4 solution is obtained. Purified Na_2WO_4 is converted to high purity APT either by liquid ion exchange (LIX) technique /152-154/ or by preparing synthetic scheelite ($CAWO_4$) by adding calcium chloride solution, which on hydrochloric acid digestion yields APT. The onward conversion of high purity APT directly to tungsten metal is facilitated by reaction with hydrogen at 800 to 1000 °C, but the product contains large amounts of ammonia and water vapour. To circumvent inclusion of these gases in the final product, calcination of APT to obtain high purity WO_3 and then its reduction by hydrogen /23,146/ is a better route because it yields tungsten powder of much better purity, i.e., about 99.96%. Metallothermic reduction /147-149/ of WO_3 has also been attempted by using metals like Na, Mg, Ca, Al, Si and Zn, but the best yields and products have been obtained through hydrogen reduction of WO_3.

Another way to obtain high purity APT with low molybdenum content is through chlorination of wolframite /151/ or scheelite /152/ in the presence of carbon which yields oxychloride $WOCl_4$ on hydrolysis and ammonia digestion yields APT.

Schemes, other than reduction of WO_3, to obtain pure tungsten metals are (i) hydrogen reduction of WCl_6 /152/ or WF_6 /155/, the former conveniently purified by fractional distillation, and (ii) fused-salt electrolysis /146,156,157/ using WO_3 or WF_6 as the feed materials, the latter feed material yielding tungsten crystals larger than those obtained by hydrogen reduction of WO_3.

The tungsten powders, produced by the schemes mentioned above, have a purity of about 99.96%. The powders for onward fabrication or purification are compacted (at 135 to 240 MPa), sintered (at 2000 - 2400 °C) to remove C (as CO), O (as H_2O, WO_3), H and N, and finally melted by means of arc or electron beam melting and in special cases subjected to EBFZM /60,140,142/.

The work on tungsten single crystal growth has been of special interest because of unique high temperature strength of the metal. Some workers have studied the single crystal growth /60,142/ by EBFZM for evaluating certain basic physical properties of tungsten metal. Difficulties associated with EBFZM of

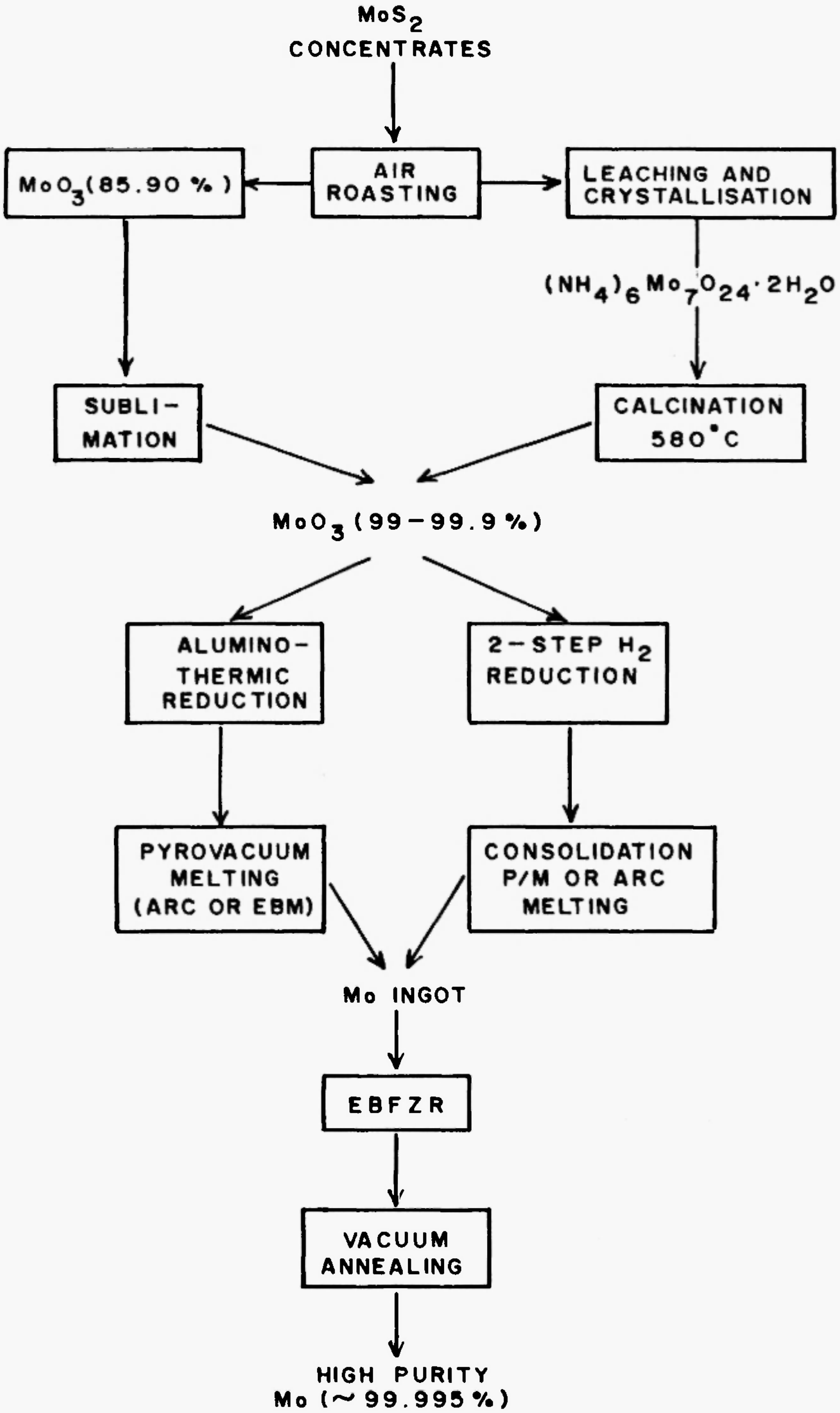

Fig. 6: Flow sheet for high purity molybdenum.

tungsten arise on account of the volatility of tungsten manifesting them as clogs in the apparatus or snapping of the specimen rod due to localised decrease of the diameter.

On the purification front EBFZM is particularly useful in removing impurities like O, Si, Al, Fe, Ni and Cu. Analytical results of high purity tungsten crystal /142/ which include measurement of oxygen content by fast neutron activation analysis and other impurity contents by spark source mass spectrometry, are given in Table 11. The resistance ratio (RR) of this material was 30,000. The highest value of RR however is 100,000 as measured by Kopetskii et al. /76/.

It may be worthwhile to refer to data given in Table 8, which were compiled by the Materials Research Corporation for impurity concentrations of zone refined tungsten metal measured by one of the latest analytical tools, i.e., gas discharge mass spectrometry (GDMS). The flow sheet to obtain high purity tungsten metal is given in Fig. 7.

PURITY ASSESSMENT

To complete any scheme to achieve ultrapurification of a material, it is imperative to carry out the purity assessment of the intermediates (compounds) and products at each and every processing stage. Today's analytical chemistry is fortunately permitted to deal with the problem of ultrahigh purity assessment as a result of the coincidence of the availability of highly sophisticated methods of analysis and the demand for materials with stringent purity requirements for use in the nuclear, space and electronics industries.

Strictly speaking, characterisation of an ultrahigh purity material envisages comprehensive evaluation, including analytical measurements of major, minor and trace chemical constituents (composition, stoichiometry and homogeneity in compounds and alloys) and physical properties (structure and defects). For this article, it would be adequate to confine to chemical purity assessment of ultrahigh purity refractory metals. Impurities in refractory metals are broadly of two types, i.e., metallic (substituted) and non-metallic (interstitial), and methods to measure both these types of impurities will be briefly described.

The conventional methods of purity analysis are inadequate to deal with the vanishingly low impurity contents, namely at ppm, ppb and ppt levels. Consequently, efforts expended to meet the pressing demands to assess the stringent purity requirements have resulted in refining and developing several analytical techniques with increased sensitivity (low detection limits), simultaneous multi-elemental (low interferences) and minimal sample (solid) quantity requirements.

More commonly employed methods for measuring trace elements in ultrahigh purity refractory metals are emission spectroscopy (ES), spark source mass spectrometry (SSMS), atomic absorption spectrophotometry (AAS), neutron activation analysis (NAA), vacuum fusion and non-specific (physical) property measurement such as electrical resistivity.

Many instrumental techniques have since come into being which use lasers, plasmas, glow discharge, ion sputtering, etc. for specimens atomisation, excitation and ionisation for the analytical spectrochemical methods. More recent techniques for ultratrace analytical measurements in bulk metals are inductively coupled plasma optical emission spectroscopy (ICP-OES), gas discharge-OES (GD-OES), inductively coupled plasma mass spectrometry (ICP-MS), gas discharge MS (GDMS), graphite furnace atomic absorption spectrophotometry (GFAAS), radiochemical separation neutron activation analysis (RNAA), instrumental NAA (INAA), charged particle AA (CPAA) and measurement of resistance ratios (RR) of the solid sample.

The usefulness of an analytical instrument depends upon its sensitivity, specificity and type of specimen to be employed. Analytical results obtained from solid form of specimen has an edge over techniques employing aqueous solutions, because of problems such as loss of integrity of the sample due to contamination from reagents, containers and reduced sensitivity on account of dilution resulting on dissolution.

OPTICAL EMISSION SPECTROSCOPY (OES)

OES has been the most extensively used method for evaluation of the trace impurity contents in high purity refractory metals. The general sensitivity of the method lies between 0.1 ppm to 1 ppm (wt), but the

TABLE 11

IMPURITY CONCENTRATIONS IN HIGH PURITY TUNGSTEN METAL (CRYSTAL), OXYGEN BY FAST NEUTRON ACTIVATION ANALYSIS (FNNA) AND OTHERS BY SPARK SOURCE MASS SPECTROMETRY (SSMS) REF. 142

Impurity element	Content - ppm (wt)
O	<0.5
C	<1.
N	<0.6
H	-
Si	<0.3
Al	<0.1
K	<0.1
Ca	<0.1
Na	<0.3
P	<0.3
S	<0.3
Mn	<0.3
Nb	<0.1
Ta	<0.1
Re	<0.1
V	<0.3
Fe	<0.1
Ni	<0.06
Co	<0.3
Cr	<0.05
Cu	<0.05
Pb	<0.1

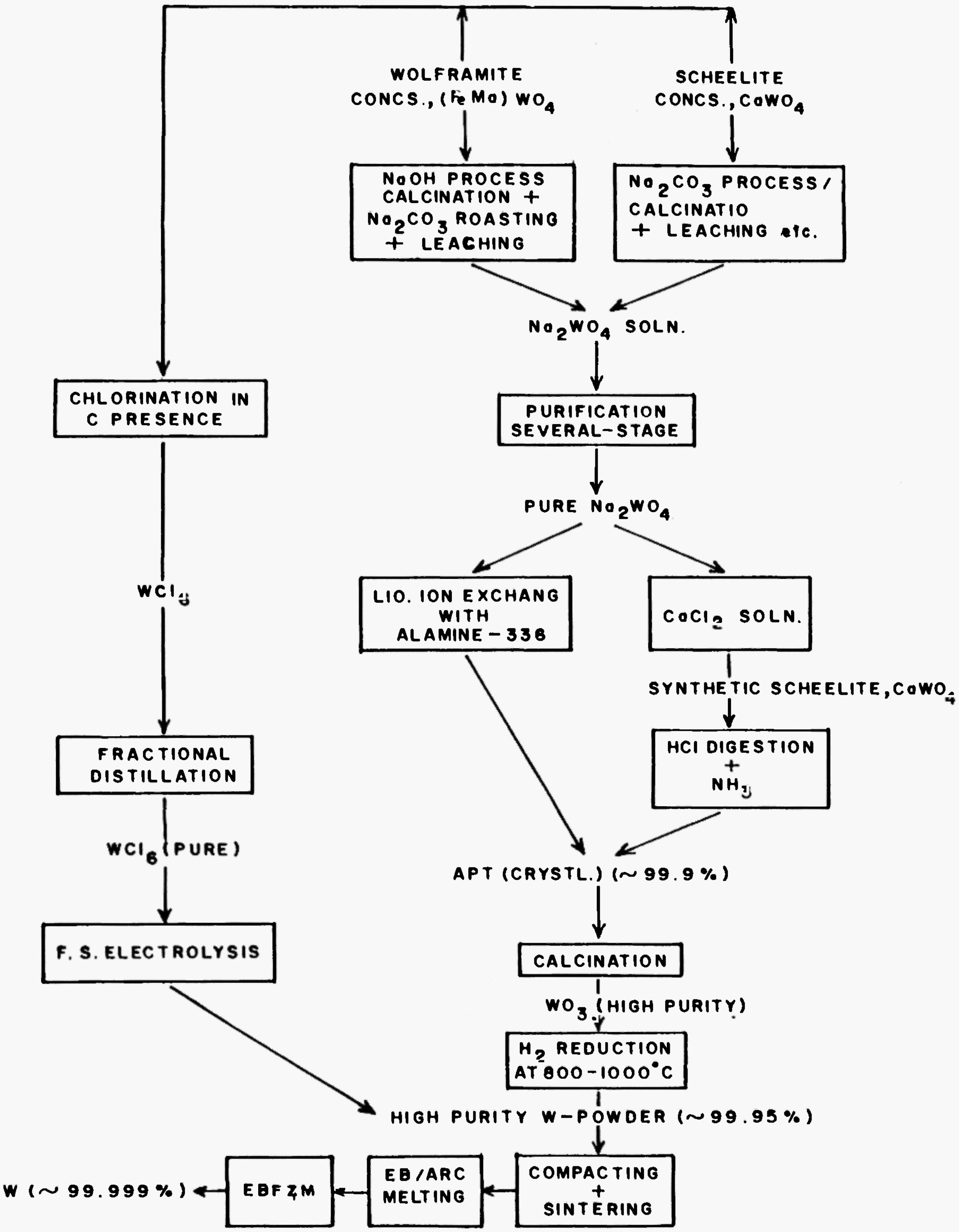

Fig. 7: Flow Sheet for tungsten.

sensitivity has been improved by using preconcentration techniques /159/ and the means of exciting the samples by ICP /160-165/ or G.D /166/. Today, ICP-OES is the most widely established technique because of its higher sensitivity, speed of analysis and a capability to provide multi-elemental analysis, and it is comparable to the NAA and MS methods in certain cases.

The OES technique consists in excitation of the atoms of the specimen by arc, spark, plasma or gas discharge and the energies on deexcitation of the electrons in the element atoms are emitted in the form of characteristic spectrum of the elements which are dispersed and recorded by means of a prism or grating spectrograph. The elements can be identified by the position (wave-length) of the characteristic spectral lines and estimated by the intensities of the lines which are a function of concentrations of the corresponding elements in the sample. The general method of OES warrants the use of synthetic standards.

ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS)

Experimentally it is equivalent to flame photometry but has higher sensitivity. It is based on the principle of selective line absorption by an atomised atom of the trace element. Its higher sensitivity is attributable to the phenomenon dependent on the ground state population rather than the excited state of the atoms in the conventional method of flame AAS (FAAS) /172-176/. The sample is aspired into a flame for atomisation and radiation of correct wavelength is passed through the flame and the absorption by the trace impurity atoms in the sample is measured photometrically. Development of the method known as a graphite furnace AAS (GFAAS) /167-171/ has resulted in substantial improvement in the direction limits by as much as two orders of magnitude for most elements. Comparison of detection limits for aqueous solutions as obtained by applying FAAS, GFAAS and ICP-OES can be made from the data given in Table 12 (after Niemax) /177/.

Basically the instrumentation for AAS comprises (i) atomiser (flame or electrothermal) for sample, (ii) light source for characteristic resonance line emission (hollow cathode or discharge lamp), a monochromator tuned to resonance line, and (iii) photomultiplier detector and radiation meter. Most of the commercially available AAS instruments these days offer facilities for solid sampling which in itself is an asset for carrying out ultra trace elemental analysis.

Essentially AAS as one-element method and measurement of simultaneous detection of multi-element warrants a continuous light source and a high resolution spectrometer with exit slits tuned to the wavelength of the resonance lines or a multi-element lamp with a low resolution spectrometer. The detection sensitivity with the use of a continuous light source is, however, lower than that of a line source. As in OES, preconcentration techniques employed for matrix-trace separation result in better detection limits for trace elements is from 0.001 ppm to 1 ppm.

MASS SPECTROMETRY (MS)

Mass spectrometers in general have been used for gas analysis and impurities in organic substances for a long time. Application of mass spectrometer to measure impurities in high purity materials was done by Hannay and Ahearn /178/ in 1954. The development of spark source mass spectrometer (SSMS), the most common form of MS, used for analysing ultrahigh purity metals, was in response to the emergent needs of determining impurities in solid materials in the 1950s. However, due to commercial availability of SSM spectrometers and the demonstration of the first laser by Maiman et al. in the 1960s, the most dramatic advances in the field of ultratrace determination in the solid state had taken place.

In essence for performing SSMS /179,180/ the solid specimen is vaporised, atomised and finally ionised by applying a high frequency (0.5-1 MHz) high voltage spark for a few microseconds. The ions formed by sparking are accelerated and, by applying traverse electrostatic and magnetic fields, are separated into mass-to-charge ratio and the mass spectrum is recorded. The highest merit possessed by SSMS, apart from being more sensitive than several other trace analytical methods, is its capability to determine practically all the elements of the periodic table, provided interferences are taken care of. With the latest instruments, the detection limits are as low as 10 ppb (generalized range of

TABLE 12
COMPARISON OF DETECTION LIMITS FOR AQUEOUS SOLUTIONS APPLYING FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY (FAAS) GRAPHITE FURNACE ATOMIC ABSORPTION SEPCTROPHOTOMETRY (GFAAS) AND ICP-OES (AFTER REF. 177)

Element	FAAS	GFAAS	ICP-OES
Ag	1	0.005	2
Al	30	0.01	0.2
As	20	0.2	2
Au	6	0.1	0.9
Ba	10	0.04	0.01
Be	2	0.03	0.003
Bi	20	0.1	10
Ca	1	0.05	0.0001
Cd	0.5	0.003	0.07
Co	6	0.02	0.1
Cr	2	0.01	0.08
Cu	1	0.02	0.06
Fe	5	0.02	0.09
Hg	200	2	1
K	1	0.002	30
Li	0.5	0.2	0.02
Mg	0.1	0.004	0.003
Mo	30	0.02	0.3
Mn	1	0.01	0.01
Na	0.2	0.01	0.1
Ni	4	0.2	0.2
Pb	10	0.05	1
Pt	40	0.2	0.9
Sb	30	0.1	15
Se	100	0.5	1.1
Si	50	0.1	2
Sn	20	0.1	3
Te	20	0.1	15
Ti	50	0.5	0.03
Tl	10	0.1	-
V	48	0.2	0.06
Zn	1	0.001	0.01

detection limits: 0.005 ppm to 1 ppm). Further improvements in the detection limits of SSMS could be achieved if the complex nature of ions produced (including not fully dissociated or multistage ionisation) are resolved.

Several other mass spectrometric instrumental techniques have been developed in response to the specific needs of ultra trace analysis of special or ultrahigh purity materials. Among these relevant to trace analysis of refractory metals are inductively coupled plasma (ICP) /181-185/ and gas-discharge (GD) /186-189,194/ mass spectrometers. The use of lasers in mass spectrometry to effect very selective ionisation and enhanced temperatures is yielding better semiquantitative analysis of specimens without the need to standards is one of the unique features of laser mass spectrometry (LMS) /190-193/.

Among the MS techniques using solid samples, namely SSMS secondary ion mass (SIMS), IPC-MC and GDMS, the last technique has become the most accepted one for bulk trace analysis of ultra purity metals /158,189, 190,194/. Measurement of metallic trace impurities by GDMS in zone refined V, Nb, Ta, Mo and W are given in Table 8 /158/. Guidoboni et al. /189/ reported by the application of GDMS, detection limits of U and Th in Ti and Al metals used in very large scale integration (VLSI) circuit fabrication up to 0.2 ppb and 0.5 ppb, respectively. Trace analysis by GDMS is conveniently and efficiently applicable to refractory metals because of the basic necessity of having the specimen as an electrically conductive or semiconductive material.

While mentioning various trace analytical spectroscopic techniques, it may not be out of place to touch upon ionisation spectroscopy which has extremely high sensitivity and selectivity. Although not directly relevant for the evaluation of the purity of refractory metals, the resonance ionisation spectroscopy (RIS) /195,196/, sputter-initiated ionisation spectroscopy (SIRISD) /197/ and laser enhanced ionisation spectroscopy (LEIS) /198-200/ have brought the sensitivities down to ppt level in routine analysis and still better sensitivities in special cases. For instance, Lawrenz et al. /200/ have reported detection limits as low as 0.008 Pg/ml and 0.0015 Pg/ml for the trace elements Ag and Pb, respectively.

NEUTRON ACTIVATION ANALYSIS (NAA)

Basically NAA /202-206/ is a radioactive tracer technique in which radionuclides are formed insitu. It can provide both qualitative and quantitative information of the elemental constituents of a large variety of samples. Activation analysis using thermal neutrons (from atomic reactors) for bombardment of the specimen to be analysed is the most commonly employed and the most developed technique. The irradiation of the sample results in the formation of several radioactive products. Typically the gamma rays, emitted either from transitions among activated nuclear energy states of the compound nucleus or from radioactive decay products, are measured by using γ-ray spectroscopy. The γ-ray energies are characteristic of specific indicator radionuclides and their intensities are proportional to the amounts of various target nuclei present in the specimen sample.

Estimation of target (impurity) atoms present in the sample can be calculated from the activation equation given by

$$A = n\phi\sigma(1-e)^{-\lambda t}/(e^{-\lambda d})$$

where A is the absolute induced activity of the specimen (disintegrations s^{-1}), n the number of atoms of target atoms, ϕ the neutron flux density (neutrons $cm^{-2}s^{-1}$), σ the neutron absorption cross section (cm^2), λ the decay constant of the radionuclide produced (s^{-1}), t the time of irradiation (s) and d the decay constant before counting (s).

The task to obtain elemental quantitative concentrations from the equation given above is rendered complex because of uncertainties such as neutron absorption cross section and the effective flux density. In practice, to circumvent such difficulties, use of a comparator is made which is irradiated under the same experimental conditions as the specimen, i.e., simultaneously, and quantity x of the impurity can be determined from

$$\frac{\text{quantity of x in specimen}}{\text{quantity of x in comparator}} = \frac{\text{measured activity in specimen}}{\text{measured activity in comparator}}$$

The irradiated specimen usually contains more than one radionuclide and hence the accuracy and the sensitivity of the method would depend on separation and distinguishing these in the radionuclide mixture. The NAA, when carried out without radiochemical separation, which is often the case, is known as instrumental neutron activation analysis (INAA), while the other to involve radiochemical separation is known as a radiochemical separation NAA (RNAA) /206-209/, is bound to lead to accurate measurements.

Table 13 shows the list of generalised sensitivities of INAA and RNAA /205/. Evidently, values given in the table indicate lower detection limits for impurities by RNAA.

It may be of interest to cite here examples of successful applications of INAA and RNAA to ultrahigh purity refractory metal Mo as given in Table 14 /145/.

The generalised range for detection limits by NAA is 10^{-11} g to 10^{-6} g/g (10 ppt to 1 ppm). NAA offers a number of distinctive advantages such as minimal risk of contamination, high sensitivities and capability of multi-elemental analysis. The method is relatively reagent free and occasionally non-destructive.

Neutron sources traditionally employed for activation are nuclear reactors, accelerators and isotopic

TABLE 13
SENSITIVITIES OF NEUTRON ACTIVATION ANALYSIS
DETECTION LIMITS IN μg/g (AFTER REF. 205)

d.limits (g/g)	INAA	RNAA
10^{-1}	Fe, Ni, Sr, Zr, Sn	Pb
$5x10^{2}$	Zn, As, Rb, Cd, Ba	
10^{-2}	Br, Mo, Ho	Fe
$5x10^{3}$	Cr, Mn, Ru, Pd, Ag, In, Te, La, Nd, Gd, Pt	S, Ca, Zr, Bi
10^{-3}	Co, Se, Sb, Xe, Ce, Yb, Ta, W, U	Mg, Si, Ti, Ni, Tl
$5x10^{4}$	Cs, Hf, Ds, Hg, Th, Np	Mo, Sn, Xe, Ce, Nd
10^{-4}	Re, Sm,Eu,Tb,Tm	Be, K, Se, Sr, Ru, Cd, Te, Ba, Pt, Zn
$5x10^{-5}$	Al, Sc, Lu, Au	Al, P, Cl, Cr, Ge, Rb, Nb, Cs, Hf, Os
10^{-5}	Ir	Na, Ar, Ga, Y, Pd, Sb, Pr, Gd, Ta, Gd, Ta, Hg, U
$5x10^{-6}$		Li, Sc, V, Cu, As, Br, Kr, I, La, Tb, W, Th
10^{6}		Mn, Co, Rh, Ag, Sm, Er, Tm, Yb, Re
$5x10^{-7}$		Ho, Lu, Ir, Au
10^{-7}		In, Dy
$5x10^{-8}$		Eu

TABLE 14
ANALYSIS OF ULTRAHIGH PURE Co BY RNAA AND INAA (REF. 47) (in g/g)

Element	RNAA	INAA
Ag	<8.9	-
Co	712	660
Cr	1940	2003
Cs	2.9	-
Cu	2400	-
Fe	14000	13800
Hf	-	13.4
Ir	<0.01	-
K	5970	-
Mn	621	-
Na	62.3	-
Ni	1000	-
Rb	<68	-
Sb	-	1350
Sc	4.6	-
Se	<3.4	-
Sn	-	4100
Ta	-	3.9
Th	44.6	41.9
U	1080	-
W	-	118
Zn	<16.8	-

(Detection limits for α-emitters, Th and U, respectively are <0.037 ng/g and <4.0 ng/g).

sources. Most commonly used neutrons are the thermal (from reactors), accelerator-produced 14 MeV neutrons through $^3H(d,n)^4He$ reaction and the intensity neutrons (sources may be based on either the spectrum fission of ^{252}Cf, Pu-Be or Am-Be mixtures producing neutrons through ^9Be (a,n)^{12}C reaction of ^{124}Sb-Be photoneutron sources produced via ^9Be (γ,n) 2^4He reaction). MeV neutrons are used in the technique known as fast NAA (FNAA) /210,211/ for specifically determining impurities such as F, O, N, P and Si etc.

With the dramatic improvements in other analytical techniques during the last couple of decades which have become competitive with NAA in sensitivity, NAA still enjoys a special status in the analytical arsenal because of its potential for blank-free and matrix-independent use.

RESISTANCE RATIO (RR)

Of the methods pertinent to measurement of physical properties (electrical resistivity, refractive index, density, absorption spectrum, internal friction, etc.) to assess the purity of metals, measurement of electrical resistivity at two temperatures is an excellent tool to determine purity concentrations.

The electrical resistivity of a metal can be conveniently divided into three components, i.e.,

$$e_T = e_{Th} + e_d + e_i$$

where e_T is the total resistivity, e_{Th} the resistivity due to thermal lattice vibrations, e_d the resistivity due to lattice imperfections (vacancies, dislocations, grain, boundaries, etc.) and e_i the resistivity due to impurity atoms. While the terms e_d and e_i are essentially temperature independent, e_{Th} is approaching zero at absolute zero temperature. Thus if we measure the resistivity near zero K, we measure a sum of e_d and e_i. Now if we use well-annealed large metal samples, the contribution of e_d, i.e., due to physical defects (vacancies, dislocations, grain boundaries etc.) can be neglected and we get a good measure of e_i contribution to the total resistivity value.

The resistivity at low temperature is, however, extremely sensitive to the amount of trace elements present in the sample. This fact gives rise to the 'RR' test which is an extremely sensitive qualitative (non-specific) method of measuring purities of 99.999% and better in metals. The usefulness of the method lies not only in the sensitivity but also in the relatively simple and rapid procedure.

Normally, resistance measurements (at low temperatures) warrant accurate dimensional requirements. This is circumvented by measuring the resistance at room temperature (298K) and liquid helium temperature (4.2K) for the same specimen and reporting the resistance ratio (RR) value at Q. The higher the RR values for a particular sample, the more enhanced the overall purity of the metal.

For this article, the best RR values for high purity refractory metals as obtained from the open literature are compiled in Table 1.

Although the RR test has the advantage of high sensitivity, higher speed and enhanced simplicity for characterisation of the ultrahigh pure refractory metals, caution must be exercised because of its inherent non-specific nature. For instance, a specific elemental impurity in question cannot be evaluated by RR measurement as different impurity atoms have vastly different contributions to resistivity. Secondly, because only impurity atoms in solid solution are effective electron-scatterers, nothing can be said about the impurity content in a precipitate or compound form. Thirdly, even for impurity atoms in solid solution, the resistance ratio is a sensitive measure of purity only when the impurity content is about 100 ppm or less. Finally, among the refractory metals, V and Nb superconduct at 4.2K, making the RR test difficult. However, the superconductivity state at 4.2K in both V /19/ and Nb /21/ metals is suppressible by applying a magnetic field and measuring the resistance value as a function of the applied field and extrapolating to zero field.

VACUUM FUSION (VF)

Interstitial impurities in refractory metals when present at lower levels pose a special challenge for their determination. To find solutions, the application of methods such as hydrogen reduction, (micro) Kjeldahl, combustion, vacuum and inert gas fusion, SSM, infrared spectroscopy, internal friction, and activation analysis has been attempted with varying degrees of success. Methods such as combustion for carbon estimation and ultrahigh vacuum fusion /212-215/ of interstitials O, N and H are preferred methods for their determination in ultrahigh purity refractory metals.

With the availability of innumerable trace analytical methods, so diverse in nature, sensitivity and selectivity, obtaining accurate and reproducible results depend on parameters such as methodology, specimen sampling, standardisation (calibration), reagents, environments (atmosphere, containers) and the analyst himself.

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