

The present status and the projected programme on niobium-tantalum metallurgy in India

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NIOBIUM and tantalum which belong to the family of refractory rare metals, have assumed great strategic importance in present day material development programmes, specially in industries like chemical and nuclear engineering, electronics and aerospace.

The use of niobium as ferroniobium contributing to carbide stabilisation in stainless steel is well established and accounts for the major demand for niobium in the world today. At the same time, niobium-based alloys have been considered excellent for high temperature service, and in particular two alloys (i) SU-16 (Nb-11W-3Mo-2Hf-0.08C), and (ii) Nb-752 (Nb-10W-25Zr)¹—have been developed for application in aerospace structure components. With its relatively low neutron absorption cross-section ($\sigma_a=1.1$ barns), compatibility both with uranium fuels and liquid metal coolants, and good high temperature strength and fabrication characteristics, niobium is also an attractive candidate for nuclear energy application, particularly in fast reactors. Also, a zirconium-alloy containing 2.5% of niobium is a potential competitor to zircaloy for structural core components in water-cooled thermal reactor systems.

Tantalum which is an equally, if not more, valuable by-product in niobium production, is corrosion-resistant to most mineral acids and will be the ideal structural material in many chemical process industries, but for its high price tag. The vast reserve of ductility and favourable electrical characteristics of tantalum account for its application as heating elements in furnaces operating in high vacuum, above 2000°C. The excellent performance of miniature tantalum capacitors—characterised by high capacitance in a wide temperature range, low leakage current and good rectification properties—has also created a great and growing demand for tantalum in the electronic industry.

A survey on the pattern of utilization of both niobium and tantalum and their alloys indicates that in United States alone the consumption of niobium amounted to about 1250 tons in 1965.² For the same year, the ferro-alloy consumption figure was reported around 1000 tons. In our country, there exists a definite

SYNOPSIS

The paper surveys the development programme carried out at the Bhabha Atomic Research Centre on the chemical treatment of Indian columbite-tantalite ores for the extraction of niobium and tantalum values, separation of pure niobium and tantalum compounds by solvent extraction, preparation of the consolidated metallo-thermic reduction of the pure oxides and preparation of ferro-niobium by alumino-thermic reduction of niobium concentrates. Purification of the as-reduced metals by electron beam refining and fabrication of sheet and wire products have also been examined.

In order to meet the immediate requirement of tantalum capacitors, conditions have been optimised on the preparation of high purity tantalum powder by sodium reduction of K_2TaF_7 , and the high vacuum, high temperature sintering of tantalum compacts. Proposals have been finalised for the setting up of a production capacity of 5 00 000 tantalum anodes (=1 ton of tantalum) per year, as part of a Special Materials Project at Hyderabad. The possibility of converting the by-product niobium fraction partly into ferro-niobium and partly to pure niobium metal powder is under consideration.

demand for tantalum as capacitor material in the electronics industry, estimated at 5 tons/year by 1975.³ Potential demands for niobium or its ferro-alloy have not yet been specified, but with the growth of the alloy steel industries a sizable requirement is foreseen.

Natural occurrence

Niobium and tantalum almost occur together in nature, in the form of mixed oxides, corresponding to the general formula (Fe, Mn)[Ta, NbO₃]₂. Minerals, with widely varying ratios of niobium to tantalum, iron and manganese are encountered in this family. The minerals are known as columbites when the predominant component is niobium and as tantalites when the tantalum is the more abundant constituent. For niobium alone, pyrochlore (NaCaNb₂O₆F) is another important source mineral, found in countries like Canada, Brazil and Norway. Most of the niobium

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and tantalum metal produced today is extracted from columbite-tantalite ore obtained from Africa, Brazil and Australia. In India small quantities of columbite-tantalite minerals are known to occur in the pegmatites, in the mica belt in Bihar, Rajasthan and Madhya Pradesh. A good stock-pile of this ore has been accumulated mainly as a by-product of mica mining operations. A typical composition of the ore is given in Table I. In view of the growing importance of these two metals, an intensive survey of the mineral reserves and the development of economic flow-sheets for the process metallurgy of these two metals is of urgent importance.

TABLE I Analysis of Indian columbite-tantalite ore

Constituents	Weight %
Nb ₂ O ₅	46
Ta ₂ O ₅	21
Fe ₂ O ₃	17
MnO ₂	6
TiO ₂	5
SiO ₂	2

The investigations carried out at the Bhabha Atomic Research Centre, Trombay, on the development of the process metallurgy of niobium and tantalum—described in this paper—relate to the chemical treatment of the Indian columbite-tantalite ores, separation of pure niobium and tantalum by solvent extraction, preparation of suitable intermediates for the metal production, examination of the various possible metal reduction routes and finally the consolidation and purification of the as-reduced metals. The paper outlines the salient achievements to date in this programme.

Separation of niobium and tantalum

The fractional crystallisation method developed by Marignac, utilising the difference in solubilities of the potassium double fluorides of niobium and tantalum is effective mainly for the purification of tantalum. Subsequent preparation of the pure niobium salt from the mother liquor is cumbersome, requiring many controlled precipitation stages. The more versatile method based on liquid-liquid extraction, for producing high purity niobium and tantalum has virtually superseded the classical Marignac's process in industrial practice. In this process, a suitable organic phase is brought into contact with an aqueous phase, containing the fluoro-salts of niobium and tantalum at controlled acid concentrations. By a judicious control of the acidity in the aqueous phase, pure niobium and tan-

talum (free of other contaminants) can first be transferred to the organic phase; then niobium selectively scrubbed from the organic phase and finally the tantalum-laden organic can be stripped with water to obtain the pure tantalum fraction. Utilising this principle, conditions have been optimised at the Chemistry Division of the Bhabha Atomic Research Centre for the solvent extraction separation of niobium and tantalum, using different solvents like methyl isobutyl ketone and tributyl phosphate, in HF medium.^{4,5,6} Pure oxides of niobium and tantalum as well as the potassium double fluorides of the elements are available from the current pilot plant operations.

Reduction to metal

A great deal of research and development work has been reported in the literature^{7,8,9} on the extractive metallurgy of niobium and tantalum. The available processes can be classified into the following groups: (1) reduction of oxides by active metals and non-metals, (2) reduction of halides and double halides by metals and non-metals, (3) fused salt electrolysis of halides and double halides and (4) thermal decomposition of halides.

It may be mentioned here that chlorides of the most of the refractory metals such as niobium and tantalum are extremely hygroscopic and present problems in preparation, handling and storage. The double fluorides are less hygroscopic in comparison, but then one has to reckon with the cost of fluorine and fluorinating agents which continue to be too high for easy acceptance. From these considerations, the oxides appear to be more suitable intermediates and the oxide reduction route is economically more attractive.

The general equation for the reduction of oxides of niobium and tantalum with another metal can be represented as



where M stands for either niobium or tantalum, and R the metal reductant. The standard free energy change for the reaction at any temperatures

$$\Delta F_T^\circ = \Delta F_{R_yO_5}^\circ - \Delta F_{M_2O_5}^\circ$$

being the difference in the standard free energies of formation of the relevant oxides at the particular temperatures. It is obvious that at any temperature the higher the free energy (i.e. the more negative) of formation of the reductant oxide the greater the feasibility of the reaction—the greater the driving force. Thus from a knowledge of the free energy of formation of oxides, the appropriate reducing agent can be selected. On this consideration calcium, aluminium and magnesium are the most effective reductants for niobium and tantalum oxides. The free energy and enthalpy changes for the various oxide reduction reactions are given in Table II.

With the essential constraints that the product does not get alloyed with reductant metal and the metal and slag phases should be easy to separate, calcium

TABLE II Standard enthalpy and free energy changes in the reduction of the oxides of niobium and tantalum with calcium aluminium and magnesium^{10, 11}

Reaction	H° _{298°K} (K. Cal/mole of the oxide)	F° _{1000°K} (K. Cal/mole of the oxide)	Boiling point of the reductant (°C)	Melting point of the slag (°C)
Nb ₂ O ₅ +5 Ca=2 Nb+5 CaO	-298	-482.6	1440	2600
Ta ₂ O ₅ +5 Ca=2 Ta+5 CaO	-365	-246.3		
Nb ₂ O ₅ +10/3 Al=2 Nb+5/3 Al ₂ O ₃	-210	-394.6	2450	2040
Ta ₂ O ₅ +10/3 Al=2 Ta+5/3 Al ₂ O ₃	-177	-158.3		
Nb ₂ O ₅ +5 Mg=2 Nb+5 MgO	-263.5	-443	1107	2900
Ta ₂ O ₅ +5 Mg=2 Ta+5 MgO	-230.5	-206.3		

and magnesium are superior to aluminium. Calcium is further preferable to magnesium on the grounds of its higher boiling point.

Production of niobium and tantalum powders by calcium reduction

Niobium and tantalum have been produced by calcio-thermic reduction of their respective oxides at 950°C in an argon atmosphere, in presence of calcium chloride.¹² The incorporation of calcium chloride as the heat-sink is found to be essential especially in view of the relatively high heat of reaction. The heat-sink prevents, to a great extent, the excessive sintering of the reduced metal powder and possibly, to a minor extent, also acts as scavenger for oxygen in the system. Reduction tests on both niobium and tantalum oxides with 50 per cent excess of calcium over the stoichiometric and in presence of 1.5 mole of CaCl₂ (per mole of oxide) have yielded the respective metal powders at close to 90 per cent of the theoretical yield. The metal powders after reduction are freed from calcium oxide-chloride slag by acid leaching. Typical analysis of calcium reduced tantalum and niobium metal powders are shown in Table III.

Leaching operations for obtaining the highly reactive metals, such as niobium and tantalum, normally lead to pick up of impurities like oxygen, nitrogen and hydrogen, in addition to unavoidable metal loss. These difficulties can be avoided if the metal can be produced directly in massive form, well separated from the slag.

Production of massive niobium and tantalum metals by calcio- and alumino-thermic reduction

For obtaining massive metals of niobium and tantalum from their respective oxides it is essential to have reductants with high heat of reaction and the reduction conditions should conform to effective heat utilisation. Near-adiabatic conditions are achievable in the bomb reduction techniques developed for the purpose.

TABLE III Analysis of niobium and tantalum powders

Impurities (in ppm)	Powder sample	
	Tantalum	Niobium
Al	80	100
Bi	<10	<10
B	4	5
C	300	500
Ca	<10	<10
Cu	<25	<25
Fe	210	300
Mg	150	100
N	—	200
Ni	55	60
Nb	300	—
O	6000	10150
Pb	50	80
Si	500	600
Sn	<10	<10
Ta	—	400
Ti	<50	<50
Zr	<50	<50

It will be clear from Table II, that more heat may be expected to be released when calcium is used as the reducing agent in preference to either magnesium or aluminium. In view of the high melting points of niobium (2468°C) and tantalum (3000°C), auxiliary reactions for extra heat contribution are necessary in bomb reductions to improve metal recovery. Sulphur has been chosen which reacting with the reductant calcium contributes the extra heat.

The reduction experiments have been carried out in magnesia lined steel bombs. The experimental details and procedures have been described elsewhere.^{13,14,15,16} The reaction between calcium and sulphur, besides supplying extra heat, triggers the main reaction at a comparatively low temperature. Studies have initially been carried out on the reduction of 50 g lots of niobium pentoxide per batch and later extended to 500 g lots. In a typical run with 500 g of niobium pentoxide, 40 per cent of calcium in excess of the stoichiometric and 20 per cent of sulphur by weight of the oxide and at a bomb wall temperature of 500°C, a niobium metal button yield of 83% has been achieved. In similar tests with tantalum pentoxide the tantalum metal yields have been found to be 70 per cent. The analyses of the massive niobium and tantalum biscuits (as-reduced) are shown in Table IV.

TABLE IV Analysis of calcium-reduced niobium and tantalum metal biscuits

Impurities (in ppm)	Sample	
	Calcium-reduced niobium biscuit	Calcium-reduced tantalum biscuit
Al	150	10
B	0.5	0.5
C	850	600
Ca	7 000	2 400
Co	5	10
Cr	250	—
Cu	250	10
Fe	1 000	500
Mg	250	200
N	150	110
Nb	—	600
O	650	1 080
Pb	10	25
S	810	600
Sb	8	25
Si	250	600
Sn	8	10
Ta	500	—

Compared to other reductants such as magnesium and aluminium, the cost of calcium runs quite high. The high vapour pressure of magnesium and its low heat of reaction are arguments against its use as a reductant, especially in a closed system when massive niobium and tantalum are to be obtained. While aluminium was also hitherto considered unsuitable because of its tendency to alloy both with niobium and tantalum, the development of high vacuum melting techniques (such as electron beam melting) has significantly altered the picture and removal of aluminium from the reduced metal can now be achieved by melt-refining processes. In comparison with calcium, at first sight, it would appear difficult to obtain massive niobium and tantalum through aluminothermic reduction. The lower melting point of Al₂O₃ than CaO is however an advantage, and the fluidity of the slag can be further improved by so composing the charge that a low melting eutectic Al₂O₃-Al₂S₃ (Melting Point=1100°C) is formed during reduction. With these considerations aluminothermic reductions of oxides of niobium and tantalum have been investigated at Trombay.

The test conditions for the aluminothermic reduction of oxides of niobium and tantalum are essentially the same as in calciothermic reduction. In these tests again a small mixture of calcium and sulphur has been incorporated in the charge for initiation of the thermite reaction at a relatively low temperature of about 450°C. The reduction of tantalum pentoxide has been examined to establish the influence of the following process variables: (i) scale of reduction (100, 200, and 500 g of the oxide) and (ii) the proportion of aluminium added in the charge (100, 90 and 80% of stoichiometric). In a typical experiment with a charge consisting of 500 g of Ta₂O₅, 115.5 g of aluminium and 24.5 g of sulphur, cleanly separated massive tantalum metal weighing 360 g has been obtained, corresponding to a yield of 88 per cent.

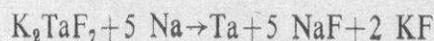
Unlike in thermite reductions of Ta₂O₅, incorporation of sulphur has been found to be unnecessary for niobium oxide reduction. Straight reduction of niobium oxide with stoichiometric aluminium has resulted in massive niobium metal yield, 90 per cent of theoretical. The analysis of the as-reduced samples of niobium and tantalum appears in Table V.

TABLE V Analysis of thermitically reduced massive niobium and tantalum metal

Sample	Impurities (%)				Hardness (DPH)
	Al	C	N	O	
Aluminium-reduced niobium button	2.82	0.023	0.04	0.81	380
Aluminium-reduced tantalum button	1.08	0.025	0.035	0.74	—

Sodium reduction of potassium tantalum fluoride

Calcium-reduced tantalum metal powder is unsuitable for the production of tantalum capacitors where specifications on purity, particle shape and size distribution are stringent. Capacitor grade tantalum powder is better produced by sodium reduction of the double fluoride. The main reaction can be represented by the following equation :



The reaction is stated to be self-sustaining accompanied by a release of 700 K.Cal of heat per kilogram of the salt and the reductant.¹⁷ The reduction reaction, with the charge consisting of alternate layers of sodium and double fluoride of tantalum, both ensured to be moisture-free, can be carried out in the open or the closed container. Any moisture, if present in the charge would react with sodium during reduction releasing hydrogen which in presence of entrapped air is likely to form an explosive mixture and may result in surging out of the entire charge. This is specially dangerous and more so for the open type of reduction technique as the charge essentially contains molten droplets of reactive sodium. As a safeguard against these and also from the point of view of the product purity, sodium reduction of K_2TaF_7 is being practised in an enclosed inconel-lined stainless steel reactor. The charging of the reactor is done in dry argon atmosphere to avoid exposure to air. Reduction conditions have been optimised by¹⁸ examining the influence of the process variables such as (1) reduction temperature and soaking period, (2) composition and initial size distribution of the charge, and (3) rate of heating, on the tantalum product purity and size distribution. After the completion of the reduction, the reduced mass is first treated with methyl alcohol to dissolve out the unreacted sodium. Further treatment of the reduced mass consists of carefully controlled series of aqueous treatment to get rid of the unreduced double fluoride, and the by-product fluorides. A typical analysis of the tantalum powder in current production at Trombay is shown in Table VI.

It may be mentioned here that possibly a better control of the reduction and also the powder shape and size distribution can be realised by adopting liquid-liquid reaction of molten K_2TaF_7 and sodium, in an agitated bath. Studies along this line are currently in progress.

Consolidation and purification of niobium and tantalum

Niobium and tantalum metals that have been obtained either in powder or in massive form are generally impure in the as-reduced condition and need to be consolidated and purified before shaping them into any usable form. The two major methods available are (a) powder metallurgical technique and (b) melting and casting in arc and electron beam melting furnaces.

TABLE VI Analysis of sodium-reduced tantalum powder

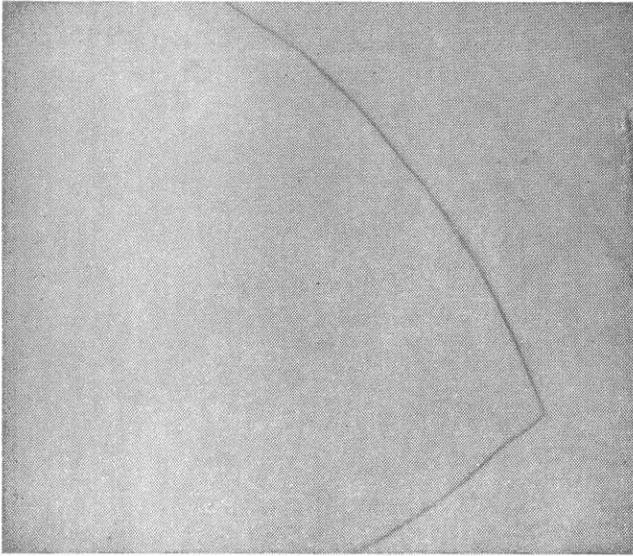
Impurities (in ppm)	
Al	50
C	200
Cr	80
Cu	10
Fe	110
Mg	10
Mo	75
N	700
Nb	100
Ni	100
O	200
Si	700
Ti	50
Zr	50

Sintering of tantalum anodes

Sodium-reduced tantalum metal powders have been used as starting material for tantalum anodes (for the electrolytic capacitor industry) through powder metallurgical techniques. The various processing steps involved in such an operation are (i) annealing of the as-received tantalum powder, (ii) crushing and grading of the annealed powder, (iii) blending of the graded powder to suit specific requirements, (iv) compacting of the mixed powder with embedded tantalum lead wire and finally (v) high temperature vacuum sintering in a tantalum resistance furnace. At each step, adequate operational controls with respect to process variables have to be strictly enforced. These conditions have been standardised at Trombay and sintered anodes are presently in regular production.

Purification by high vacuum sintering and electron beam melting

From calcium-reduced metal powders of niobium and tantalum by cold compaction and sintering in the temperature range of 2100°C under vacuum of 10^{-4} mm of Hg, sintered pellets close to 95 per cent of the theoretical metal density have been obtained, the hardness of the sintered pellets being in the range of 100-110 DPH.



1 Microstructure of electron beam refined niobium ×240

Green powder compacts have also directly been electron beam melted to yield metal of a purity comparable to that of the vacuum sintered products. The analyses of calcium-reduced and electron-beam melted metal samples are given in Table VII.

Alumino-thermally reduced niobium and tantalum metals can also be refined to ductility by electron beam

melting, but on account of the higher volatile content (which can cause disturbances in melting operations) a prior treatment either by non-consumable arc-melting or vacuum treatment has been found to be essential. Tantalum metal samples have been treated under a vacuum of 10^{-3} to 10^{-4} mm Hg at a temperature of 1600°C for removal of entrapped sulphides, occluded gases and other volatile matter, and the resulting sponge tantalum metal further refined by electron beam melting. Niobium metal samples, on the other hand, have been non-consumably arc-melted under a low pressure of argon atmosphere before the final melt-refining step. Table VII records the purifications achieved in these processes.

The micro-structures of electron beam melted niobium and tantalum are characterised by their uniform cleanliness and reveal a considerably coarse-grained structure, free of any inclusions or precipitates. A typical micro-structure of electron beam refined niobium metal is shown in Fig. 1. The electron beam melted metal samples have been further cold-worked to various forms, such as sheets, strips, wires and wire-rods without the requirement of any intermediate annealing. Fig. 2 shows a photograph of electron beam melted tantalum metal, fabricated products and the sintered tantalum anodes.

Production of ferro-niobium

Processes have also been developed at Trombay on the production of ferro-niobium, starting both with the

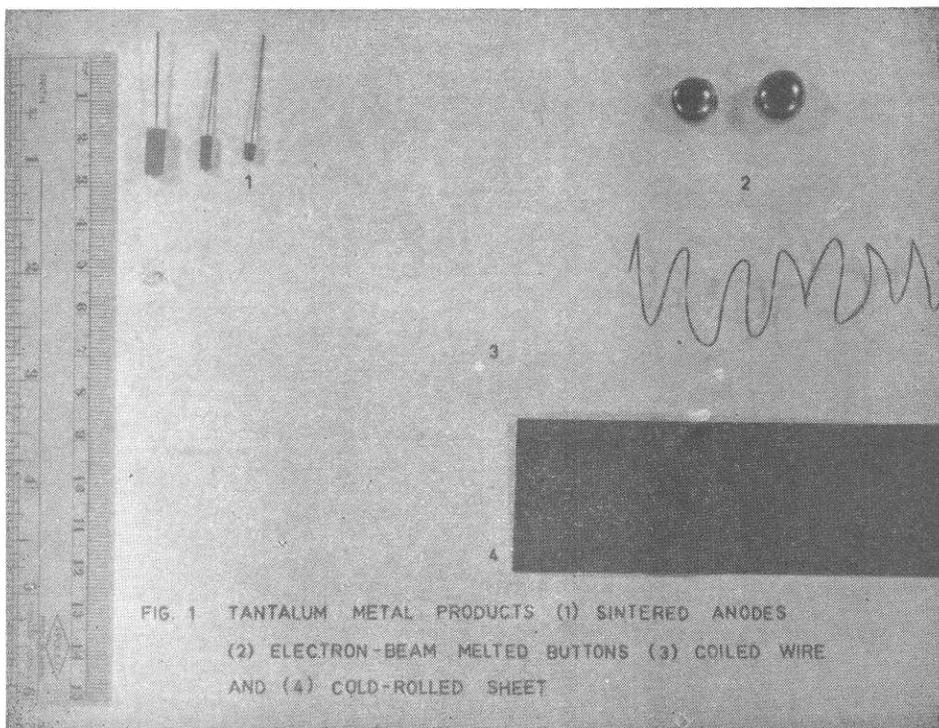


FIG. 1 TANTALUM METAL PRODUCTS (1) SINTERED ANODES (2) ELECTRON-BEAM MELTED BUTTONS (3) COILED WIRE AND (4) COLD-ROLLED SHEET

2 Fabricated tantalum metal products



3 A typical ferro-niobium 'biscuit' produced from Indian columbite concentrate

TABLE VII Analysis of electron beam melted niobium and tantalum sample

Impurities (in ppm)	Metal reduction route			
	Ca-reduced Nb metal	Ca-reduced Ta metal	Al-reduced Nb metal	Al-reduced Ta metal
Al	100	< 10	50	< 50
B	0.5	0.5	—	0.5
C	96	96	120	155
Ca	500	350	—	—
Co	5	< 10	—	< 10
Cr	20	—	—	—
Cu	10	10	—	< 10
Fe	150	10	—	15
Mg	150	10	—	< 10
N	99	80	50	35
Nb	—	< 500	—	< 500
O	520	150	200	< 140
Pb	8	10	—	< 10
S	200	< 10	—	< 10
Sb	5	< 25	—	< 10
Si	150	< 100	—	—
Sn	8	10	—	< 100
Ta	500	—	—	< 10
W	—	—	—	—
V	—	—	—	200
				< 50
Hardness (DPH)	120	95	90-100	80

columbite-tantalite ore and the niobium-rich fraction achievable from tantalum separations and using aluminium as the reducing agent. Both closed bomb and open reactor reductions have been investigated, the latter being necessary for larger batches. In the closed bomb tests (on 1 kg scale), with the incorporation in the charge chemical triggers like Ca-S, Al-BaO₂, Mg-KClO₃, the alumino-thermic reduction could be initiated by external heating to a temperature of about 900°C.²⁰ In the open reactor, on the other hand, it has been possible to carry out the reduction with as much as 10 kg batch of the concentrates, initiating the reaction by internal priming without external heating. Fig. 3 shows a typical ferro-niobium alloy button produced by the open reduction technique.

Conclusions

The foregoing survey would serve to highlight the special chemical, metallurgical and technological problems encountered in the production of high purity niobium and tantalum metal products, starting with the complex columbite-tantalite ores. With the success achieved in the development programme at Trombay, plans have been finalised for the setting up of a tantalum capacitor industry at Hyderabad, initially on a scale of 1 ton/year. It is proposed to establish an outlet for the niobium by-products either in the form

of ferro-niobium for the steel industry or as pure niobium (or its alloy) for the nuclear and aero-space industry.

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