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**SEPARATION OF TUBALLOY FROM
METALLIC TANTALUM**

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SEPARATION OF TUBALLOY FROM METALLIC TANTALUM

Standard procedures of putting tantalum into solution involve either digestion with hydrofluoric-nitric acid mixtures, or a bisulfate, carbonate, or peroxide fusion (1,2,3). Neither of these processes lend themselves well to larger scale routine work. The pentachloride of tantalum, on the other hand, can easily be dissolved in hydrochloric acid and can be prevented from hydrolyzing by dilution with dilute ammonium bifluoride solution in sufficient quantity to complex the tantalum. This pentachloride is readily prepared (along with tuballoy chlorides) by passing chlorine gas over the metallic tantalum, at 350-400°C, and collecting the sublimate.

Tuballoy is completely removed from the tantalum in the fluoride solution by a double precipitation of tuballoy tetrafluoride obtained by reduction with stannous chloride. The second precipitation, to remove the last traces of tuballoy is made complete by the co-precipitation of calcium fluoride which carries down the last traces of tetrafluoride which tend to form colloids or sols. These two precipitation leave less than one part per million of tuballoy in the solid Ta_2O_5 obtained by adding ammonia to the filtrate.

the tetrafluoride precipitates are ignited and then taken up in nitric acid to give clear fluoride-free solutions on which dituballate precipitations are made. This accounts for by far the largest percent of the tuballoy. The CaF_2 - TF_4 precipitates are ignited, digested with perchloric acid, and the calcium dituballate precipitated with ammonia. These calcium dituballate precipitates are dissolved and then reprecipitated several times with ammonia until relatively free of calcium. The ammonia filtrates are passed through a $Ca(OH)_2$ column which effectively removes the last traces of tuballoy held in solution presumably by dissolved carbon dioxide. when this column has collected sufficient calcium dituballate to warrant recovery it is dissolved in nitric acid and calcium dituballate again precipitated with ammonia.

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The various solid residues which may contain small amounts of tuballoy are ordinarily digested and extracted with nitric acid.

A control check is run on all phases of the process by means of the fluorescent method of analysis (4) which has been standardized for the samples encountered in the process. This method has proven exceedingly satisfactory.

Details of Procedure

1. Chlorination: A pyrex boat containing 300 grams of metallic tantalum is inserted into the chlorinator (Fig. 1) and the temperature rapidly raised to 350-400°C in a slow stream of chlorine gas. The gas rate is then increased to 2-3 liters per minute and the reaction continued for about 3½ hours. After cooling the reactor is taken apart and stoppered with standard taper caps while the $TaCl_5$ is rapidly transferred into tared 4 liter beakers and weighed. The reactor is then recharged giving a total time cycle of 6-8 hours.

(It is necessary to wash out the reactor every few days, with dilute NH_4HF_2 solution, as considerable tuballoy accumulates in the reaction chamber as TO_2Cl_2 formed from the oxygen in the chlorine).

2. Solution of the mixed chlorides: ½ ml conc. hydrochloric acid per gram of $TaCl_5$ is added slowly to the chlorides and the resulting solution warmed to room temperature. Then, at 70°C, 4 ml of 25% NH_4HF_2 solution for each gram of $TaCl_5$ is added with stirring.
3. Reduction and Precipitation: 20 ml 2M $SnCl_2$ solution is then added and the resulting solution digested for two hours at 85-95°C without allowing boiling to occur. A little macerated filter paper is added and the solution cooled to room temperature or lower. The precipitate is filtered off by gravity on fluted paper and washed thoroughly with cold water.
4. Co-precipitation: 20 ml 5M $CaCl_2$ is added to the filtrate which has

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been heated to 80°C and the resulting solution digested for one hour. Again macerated filter paper is added and the solution cooled, filtered and washed as above.

5. Tantalum precipitation: At this point the filtrate from the second fluoride precipitation is tested for tuballoy by the fluorescent method. If the tuballoy present in this filtrate is not considerably less than one part per million the calcium co-precipitation is repeated. Otherwise, 1200 ml conc. ammonium hydroxide is added with stirring and the resulting precipitate washed by decantation at least three times and filtered through a Buchner. After drying at 150°C another test for tuballoy is made.
6. Tuballoy recovery: The main bulk of the tuballoy is contained in the first tetrafluoride precipitate. Usually three such batches are combined and charred in a platinum dish for 3 hours at 300°C, and then ignited at 800°C for 5 hours. Then cool 25 ml conc. nitric acid is added and after a short digestion 300 ml water is added and the solution brought to a boil, cooled, filtered and washed with water. The filtrate is diluted to 700 ml with water and the pH adjusted to 2.3-2.5. After boiling 10-15 minutes the solution is cooled and conc. ammonium hydroxide added until ammoniacal. Again the mixture is heated, cooled, and then filtered and washed with boiled CO₂ free water. This precipitate is dried, charred and ignited in a platinum crucible at 800°C and then weighed. This ash is taken up in nitric acid and filtered and washed. The filtrate contains the tuballoy as relatively pure TO₂(NO₃)₂. The residue is ignited and weighed in the same platinum crucible. The difference between these two weights gives the amount of T₂O₃ in solution as the nitrate.

Summary: A method is described for quantitatively recovering tuballoy from metallic

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tantalum (as used K filaments) in the form of relatively pure Ta_2O_5 leaving less than one part per million of tuballoy in the crude solid Ta_2O_5 recovered. Approximately 0.6 percent of the used tantalum filaments is recovered as tuballoy. The method involves a chlorination of the tantalum, to put it readily into solution; precipitation of tuballoy as the tetrafluoride, made quantitative by a second co-precipitation with calcium fluoride; and recovery of the tantalum as Ta_2O_5 from the filtrate by precipitation with ammonia.

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Fig. 1

All-Glass Chlorinator

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Flowsheet TANTALUM-TUBALLOY SEPARATION I
Fig. 2

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