

- [54] **PRODUCTION OF NIOBIUM AND TANTALUM**
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- [58] **Field of Search** **75/84**

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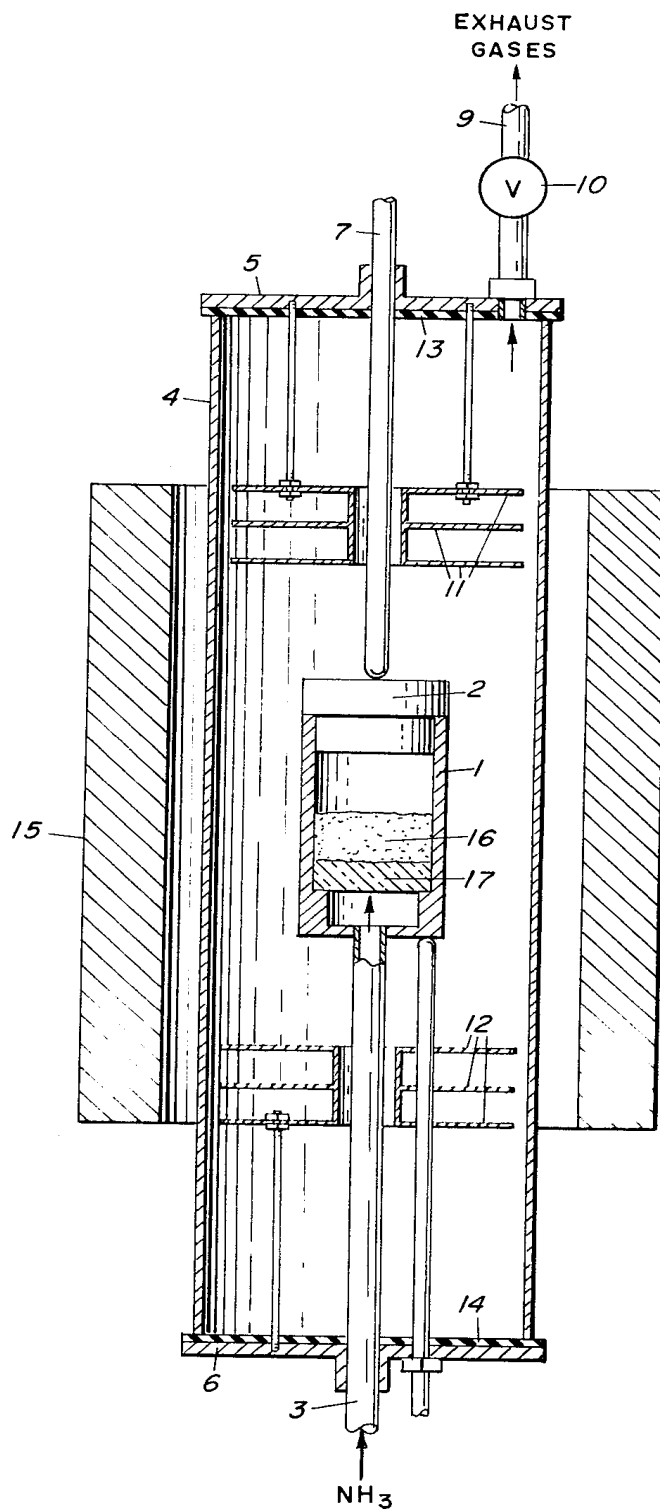
[57] **ABSTRACT**

Niobium or tantalum metal is produced by a process comprising (1) reaction of the corresponding oxide with ammonia to form the nitride and (2) decomposition of the nitride at elevated temperature and reduced pressure to form the metal. In the case of niobium, the reaction between the oxide and ammonia is preferably carried out in two stages, with initial formation of an oxynitride phase at a temperature of about 650° to 850°C, and subsequent further reaction of the oxynitride with ammonia at a temperature of about 1,100°–1,500°C to form the nitride phase.

6 Claims, 1 Drawing Figure

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PRODUCTION OF NIOBIUM AND TANTALUM

The object of the present invention is the production of niobium or tantalum metal from the respective oxide. Prior art techniques for production of these metals include carbothermic reduction of the oxide, metallothermic reduction of the oxide, hydrogen reduction of halides, metallothermic reduction of halides, and electrolysis of molten salts.

Carbothermic reduction involves the preparation of the carbide, followed by solid-solid reaction with the oxide, generally in the form of briquets, at high temperature under vacuum to remove the carbon monoxide produced. This technique is limited to a batch-type process, and tends to increase the probability of carbon-contamination of the resultant metal. Metallothermic reduction of the oxide with aluminum, calcium or magnesium also is limited by being a batch process. In this process, an alloy is produced, which must then be heated to boil off the alloy constituent.

Processes involving the metallothermic or hydrogen reduction of the halides suffer from high costs in halide preparation and difficulties of handling these reactive, hygroscopic materials which hydrolyze readily with water present in the atmosphere to form corrosive hydrohalogen acid vapors. The resultant product then becomes contaminated with undesirable oxygen.

Electrolysis of molten salts suffers from some of the disadvantages mentioned, above, for reduction of the halides. In addition, this method is generally not economic on a large scale because it presents engineering difficulties in handling and transferring of the reactive salts and cathode product.

It has now been found that the metals may be produced by means of an efficient and economical process involving reaction of the respective oxides with ammonia to form the nitride, and subsequent decomposition of the nitride at elevated temperature and reduced pressure.

It has also been found that the efficiency of such a process is, in the case of niobium, substantially improved by means of a two-step nitriding operation. In this operation the oxide is initially converted to an oxynitride intermediate by reaction with ammonia at a temperature of about 650° to 850°C, and the intermediate is then converted to nitride by further reaction with ammonia at a temperature of about 1,100° to 1,500°C.

The process of the invention will be more specifically described with reference to the FIGURE. The preferred reactor for carrying out the metal oxide-ammonia reaction is a vertical, flow-through reactor of the type illustrated in the FIGURE. This type of reactor provides a highly efficient and continuous reaction, thus obviating one of the chief disadvantages of the prior art processes, i.e., the necessity of employing batch processes. The apparatus of the FIGURE is not, however, an essential aspect of the invention, and any apparatus providing adequate reaction conditions, such as temperature, gas-solids contact, etc., may be used.

The reaction of the FIGURE consists of a hollow cylindrical vessel 1 fitted with a porous lid 2 and an ammonia gas inlet tube 3. The reactor may be constructed of various materials, including stainless steel, molybdenum, nickel, alumina, graphite, mullite, zirconia and quartz. Although any of these materials may be used, the rate of nitriding may be effected by the reactor material, in that it influences the ammonia decomposition equilibrium and, consequently, the overall reactivity of

the gas. Accordingly, optimum reactor material may vary with the type of feed material, temperatures employed, size and configuration of reactor, etc., and is best determined empirically.

Lid 2 is composed of a like material, and is sufficiently porous to permit passage of gaseous reaction products, i.e., nitrogen and water vapor, and minimize entrainment of sample in the gas stream. Suitable pore sizes will usually range from about 60 to several hundred microns, with a percent porosity of about 25 to 50.

The reactor assembly is contained in tube 4, of alumina or other impervious ceramic or metal material. The ends of this tube are closed via end plates 5 and 6 of similar materials, with openings to provide for the ammonia gas inlet tube, as well as for thermocouples 7 and 8 and exhaust gas outlet tube 9 including valve 10. The valve serves to control the flow of the exhaust gases. The end plates are also fitted with heat baffles 11 and 12 which serve to minimize heat losses due to radiation at the higher temperatures. Gaskets 13 and 14, of synthetic rubber, provide an essentially air-tight seal between tube 4 and the end plates. Heat is supplied via furnace 15, which may comprise any conventional construction such as wire-wound elements.

The metal oxide feed 16 is supported on a porous support 17, the composition of which is preferably similar or identical to that of the reactor. E.g. if the reactor is a metal, such as stainless steel, a nickel-felt pad may be used. With an alumina reactor, an alumina frit is preferable. Pore size of the porous support should be sufficient to permit passage of the gaseous ammonia reactant at the desired flow rate. Generally, pore sizes of about 40 to 200 microns are satisfactory.

Essentially anhydrous ammonia gas, containing no more than about 0.01 percent water, is fed to the reactor via inlet tube 3 at a space velocity of about 3,600 to 6,000 hr.⁻¹ The ammonia gas may also contain small amounts of its decomposition products, i.e., nitrogen and hydrogen, as well as inert gases, although the reaction rate will usually be somewhat less than that with essentially pure ammonia.

The feed material in the process of the invention consists of the pentoxides, Nb₂O₅ or Ta₂O₅, or suboxides in the case of niobium, e.g., NbO₂. They are available commercially as powders of mesh size of about -325.

When a one-stage nitriding reaction is employed, a temperature of about 1,100° to 1,500°C and a reaction time of about 40 to 50 hours is usually required. Optimum values of these variables will, however, depend on the type of reactor, nature and amount of the feed materials, purity and flow rate of the ammonia gas, etc., and is best determined empirically.

As mentioned above, in the case of niobium the nitriding reaction is preferably carried out in two stages. In the first stage, an oxynitride is formed by reaction at a temperature of about 650° to 850°C for a period of about 2 to 3 hours. This product usually contains about 2 to 4.5 percent oxygen and about 12 to 13.5 percent nitrogen. It is not, however, a stoichiometric compound, and its composition may vary considerably depending on the specific reactants and reaction conditions. In the second stage, the oxynitride is converted to nitride, NbN, by further reaction with the ammonia at a temperature of about 1,100° to 1,500°C for a period of about 2 to 3 hours. Total reaction time for maximum conversion to the nitride form by means of this

two-stage process will generally range from about 4 to 6 hours when using a small (1½ inch diameter) alumina reactor, as in the examples below. Optimum reaction time, as well as optimum temperatures may, however, vary considerably with the type of reactor employed since, as discussed above, the composition of the reactor may influence the ammonia decomposition equilibrium.

Decomposition of the nitrides to the metal is accomplished by heating at a temperature of about 1,850° to 3,000°C under a vacuum of about 100 microns or lower for a period of about 4 to 5 hours at the lower temperatures, to as little as 5 to 10 minutes at the higher temperatures. This may be accomplished by any conventional heating means capable of providing the required temperature and vacuum, in order to drive off the elemental nitrogen reaction product and leave the pure metal behind. Suitable heating means include induction, resistance, arc melting, electron beam melting, etc. Optimum temperature and time of heating will depend on the specific heating method employed, the pumping capacity of the vacuum system and size of the sample, the particular metal nitride and the degree of purity required. By selection of optimum values of temperature and time of heating, within the above ranges, a high degree of purity of the metal product, e.g. about 99.5 to 99.95 percent, may be obtained. The resulting metal products find a wide variety of uses such as preparation of steels, "getters" in high vacuum techniques, manufacture of nuclear energy equipment, alloys for use in jet engines, missiles and rockets, etc.

The process of the invention will be more specifically illustrated by the following example in which high purity niobium was prepared from niobium pentoxide.

EXAMPLE

A 7.5 gram charge of Nb₂O₅ powder was loaded into a 1½-inch I.D. vertical, flow-through alumina reactor of the type illustrated in the FIGURE. The charge was supported on an aluminum frit and was held at a temperature of 800°C. Anhydrous ammonia gas was passed

through the charge at a flow rate of 660 cc/min (STP) for a period of 3 hours to form the oxynitride, Nb(O,N).

The temperature of the reactor was then raised to 1,300°C and the Nb(O,N) reaction product was further reacted with the anhydrous ammonia at the same flow rate for an additional period of 3 hours. The resulting gray-to-silver colored nitride product, NbN, was found to contain less than 0.5 percent oxygen and 11.5 nitrogen.

The nitride product was then placed in a calcia-stabilized zirconia crucible and heated to 1,850°C under a vacuum of less than 50 microns in an induction furnace for a period of 4½ hours. The nitride was thereby decomposed to elemental nitrogen and niobium metal of a purity of 99.9 percent.

We claim:

1. A process for production of niobium or tantalum metal from the corresponding oxide comprising (1) reacting the oxide with ammonia at elevated temperature to form the metal nitride and (2) decomposition of the nitride at elevated temperature and reduced pressure to form the metal.

2. The process of claim 1 in which the nitriding reaction of step (1) is carried out in a single stage at a temperature of about 1,100° to 1,500°C.

3. The process of claim 1 in which the metal is tantalum.

4. The process of claim 1 in which the metal is niobium.

5. The process of claim 4 in which the nitriding reaction of step (1) is carried out in two stages, the first stage reaction being at a temperature of about 650° to 850°C to form an oxynitride product, and the second stage reaction being at a temperature of about 1,100° to 1,500°C to convert the oxynitride to nitride.

6. The process of claim 1 in which the decomposition of the nitride in step (2) is carried out at a temperature of about 1,850° to 3,000°C and at a pressure of less than about 100 microns.

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