Feb. 27, 1968 R. L. HOUGH 3,370,923

METHOD OF MAKING REFRACTORY METAL NITRIDE FIBERS, FLAKES AND FOIL

Filed Sept. 15, 1964

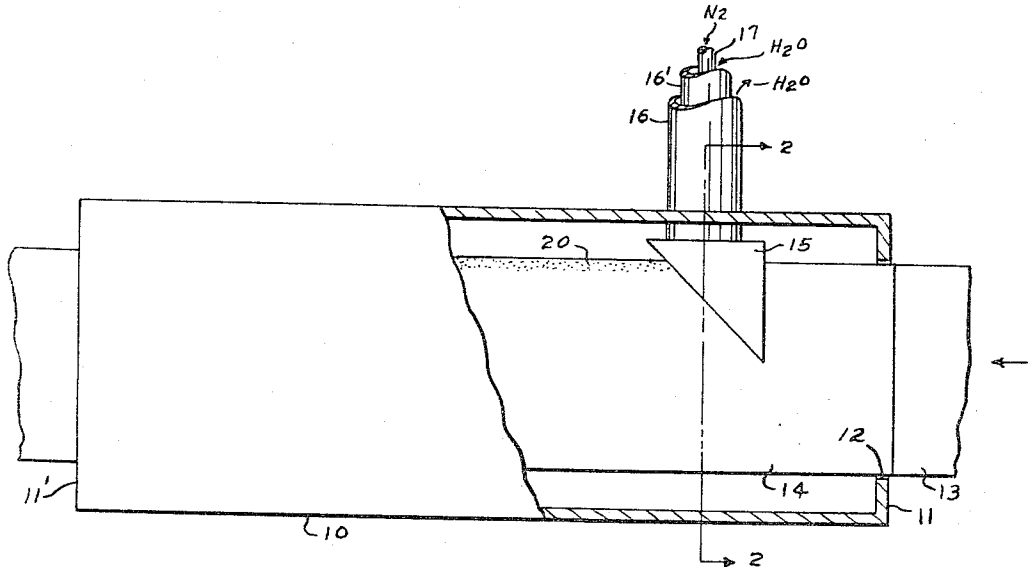


Fig-1

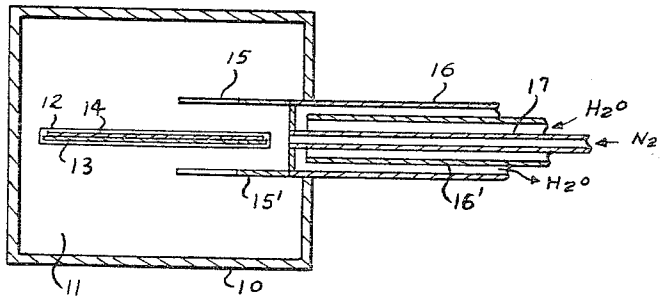


Fig-2

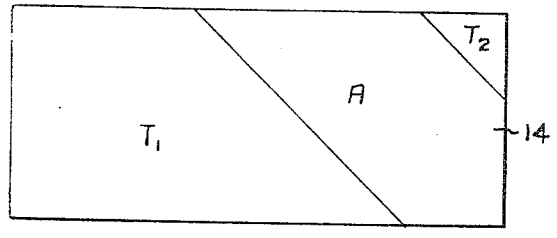


Fig-3

INVENTOR
RALPH L. HOUGH

BY Wade Kooney
Orlando Z. McCoy
ATTORNEYS

United States Patent Office 3,370,923
Patented Feb. 27, 1968

3,370,923

METHOD OF MAKING REFRACTORY METAL NITRIDE FIBERS, FLAKES AND FOIL

Ralph L. Hough, Springfield, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force

Filed Sept. 15, 1964, Ser. No. 396,780
5 Claims. (Cl. 23—191)

ABSTRACT OF THE DISCLOSURE

Method for making thin section nitride fibers, flakes or foil of a clean refractory metal selected from Nb, Ta, Ti, Hf and Zr by rolling the metal to a thinness of from 10^{-3} to 10^{-4} inch, positioning the metal on a conveyor belt chemically inert to the metal prior to the passage of the belt between an upper and a lower baffle of gas entering an oxygen-free nitriding chamber of a furnace with an atmosphere of nitrogen or ammonia wherein the baffles direct the gas flow against both the top and the bottom of the metal on the conveyor belt, and maintaining the temperature of the metal within the range of the nitriding temperature of the meal on the conveyor belt.

The invention that is described herein may be manufactured and used by or for the United States Government for governmental purposes without the payment to me of any royalty thereon.

This invention concerns a new and improved process for the nitriding of fibers, flakes and filaments of the refractory metals Nb(Cb), Ta, Ti, Hf, and Zr and to a furnace suitable for practicing the process. The material is used as missiles, nose cones, aircraft wing leading edges and the like.

The previous synthesis of metal nitrides has commonly been as coatings on substrates that are accomplished by reacting a volatile metal halide with hydrogen and with nitrogen or with ammonia, at a temperature of about between 2000 to 4000° F. by vapor deposition as a thin coating on the substrate.

The object of the present invention is to provide a new and improved method for making thin section nitride fibers, filaments, flake and foil, of a clean refractory metal. The fibers etc. are impregnated with a plastic in making reinforcement for structural and ablative material that retains its identity and its mechanical strength under great stresses and under high shear forces at high temperatures in the order of 5000° F. or 2760° C.

An illustrative embodiment of a suitable furnace arrangement in which the present invention is practiced is represented in the accompanying drawing wherein:

FIG. 1 is a side elevational view partly broken away and in section of a rectangular tubular furnace wherein the present invention may be practiced;

FIG. 2 is a diminished section taken along the line 2—2 of FIG. 1; and

FIG. 3 is a fragmentary plan view of the metal foil undergoing thermal diffusion of oxygen and nitrogen by temperature gradients.

In FIG. 1 the furnace wall **10** is of rectangular cross section and has rectangular ends **11** and **11'**. Slits **12** in the ends **11** and **11'** of the furnace **10** and dimensioned for a minimum clearance for the passage through the slits of a silica cloth conveyor belt **13** carrying strips of foil **14** the length of the furnace **10**. Adjacent to the foil input end of the furnace **10** are a pair of baffles **15** and **15'** that are positioned on opposite sides of the belt **13** and foil **14**. The baffles **15** and **15'** illustratively are cantilever supported from a pair of water conducting cooling pipes **16** and **16'** that are coaxial with a nitrogen conducting pipe **17**.

The thermal diffusion of oxygen and nitrogen in zirconium is discussed by G. D. Ruick and H. A. C. M. Bruning in volume 190, Nature, p. 1181, published in 1961.

In FIG. 3 of the accompanying drawing is indicated the fragment of the foil **14** at the input end of the furnace **10** and against a proximal edge of which nitrogen gas from the pipe **17** is discharged into the furnace **10**.

In FIG. 3, T_1 is the nitriding temperature within the furnace **10** and is higher than the temperature T_2 of the continuously moving foil **14**, as its edge passes through the nitrogen gas that is supplied from the pipe **17** to the furnace **10**. The nitrogen gas within the furnace **10** is held at a pressure that is sufficiently above ambient to maintain continuously pure nitrogen within the furnace **10**.

The foil temperature T_2 is sufficiently less than T_1 such that the nitriding of the foil does not occur appreciably at T_2 and such that in the zone A there exists a thermal gradient that causes oxygen occluded in the metal of the foil **14**, to migrate by diffusion to the cooler edge **20** of the foil **14** where it appears as a dark discoloration in the end product.

The foil **14** may be replaced by short wires that extend across the belt **13**. The gas diffusion causes a dark discoloration adjacent the ends of the wire A corresponding diffusion of gaseous impurities discolors the ends of foil or wire that is adjacent a metal support for the foil or wire.

In the described manner traces of oxygen can be eliminated from the foil or wire by thermal diffusion of the Ludwig-Soret type. This phenomenon is established in this process by the thermal gradient within the reaction zone. The oxygen diffuses to the zone of lower temperature across the thermal gradient.

Thermal diffusion is the moving of atoms of impurities, here oxygen, within a metal under the influence of a temperature gradient, with the oxygen atoms moving toward lower temperatures.

The nitriding of ultra fine wires of pure zirconium metal in the order of 0.001 inch diameter at the temperature of from 1600° F. (871° C.) to 2600° (1427° C.) is most difficult to accomplish with pure nitrogen or with ammonia, because of the reaction kinetics that are involved. The nitriding time of these ultra fine Zr wires of 0.001 inch diameter within the temperature range of from 1600° F. to 2600° F., is up to about one minute.

The reaction kinetics of nitriding zirconium are such that it is the most time consuming of the group of refractory metals, that consists of niobium, tantalum, titanium, hafnium, and zirconium. These metals are rolled to very thin foil or drawn as wire in the order of 0.001 inch thickness. The advantage of the flat rolled wire is that its edge strains are minimized by having an elliptical section or an elliptically contoured edge.

The metal thin foil or flat rolled wire is placed in a scavenged and evacuated chamber maintained in the temperature range of from 1800 to 2700° F. (982 to 1482° C.). The chamber may be a muffle furnace for batch production, or a fused quartz tubular furnace with a conveyor belt passing axially through the tube for continuous production. The furnace preferably is initially scavenged or baked out and then is evacuated. During the production of the nitrided metal, the furnace is suppled with an atmosphere of ultra pure nitrogen or ammonia at slightly above atmospheric pressures. The group of refractory metals may be illustrated by zirconium.

The nitrogen or the ammonia is procured as cylinder grade gas. Illustratively, the nitrogen is passed through a dessicant, such as a desired succession of increasingly dehydrated containers of magnesium perchlorate, for the

substantially complete removal of water vapor. The dehydrated nitrogen is cleaned of oxygen, as by being passed through a desired plurality of beds of copper turnings that are maintained about in the range of from 1400 to 1800° F. (760 to 982° C.). The resultant nitriding gas is supplied continuously as the ultra pure atmosphere in the chosen nitriding chamber.

The ultra pure nitriding gas in the chamber is passed over the zirconium or other foil, or flat rolled wire at 1800 to 2700° F., at a flow rate that is maintained at the rate of the complete nitriding of the selected refractory metal end product. The use of the long tube furnace with a conveyor system passing longitudinally through the tube requires gas baffling to prevent back diffusion of ambient gases into the reaction zone, or requires the maintaining of a closed system for the entire operation.

The nitriding process is applied to foil or wire that is about in the range of from 0.001 to 0.0001 inch thick. With the refractory metal 0.00014 inch Zr foil at 1920° F., the Zr is completely nitrided in one minute, by experimental determination. The ZrN so made had a melting point of 2980° C. or 5400° F. without sublimation or decomposition under a pressure of one atmosphere; an X-ray density of 7.349 g./cm.^{3}; a vapor pressure below 10^{-7} at 1730° C.; and a hardness of 8–9 mohs. The nitrides of Nb, Ta, Ti, and Zr are substantially chemically inert at room temperature of 22° C., being attacked only by mixtures of strong acids and oxidizing agents.

The resultant ZrN in thickness in the order of 10^{-4} inch thick was then used by being combined with a polymerized plastic such illustratively as an epoxy resin or the like, as a reinforced structural and ablative plastic composite for use at very high temperatures in the order of 2950 to 3310° C., with the exception of niobium nitride which melts at 2050° C., and of excellent thermal shock resistance. The fibrous material of zirconium nitride packed resin makes a tough and serviceable material from which are made ablative plastics to serve as the lead edges of aircraft wings and the like, by a molding operation.

It is to be understood that the details of the process that are disclosed herein may be modified somewhat without departing from the spirit and the scope of the present invention.

I claim:

1. The method of making refractory metal fibrous nitride flake by rolling a refractory metal selected from the group that consists of Nb, Ta, Ti, Hf and Zr to a thickness about in the range of from 10^{-3} to 10^{-4} inch; positioning the rolled refractory metal on top of a conveyor belt that is chemically inert to the metal, passing the metal on the belt between an upper and a lower baffle of gas entering an oxygen-free nitriding chamber of a furnace with an atmosphere selected from the group of gaseous nitrogen and ammonia at a pressure above ambient wherein the pair of baffles direct the gas flow against both the top and the bottom of the refractory metal on the conveyor belt, maintaining the temperature of the refractory metal about within the range of the nitriding temperature of the metal on the conveyor belt, and removing the nitrided refractory metal from the nitriding chamber of the furnace.

2. The method described in claim 1 wherein the conveyor belt is made of silica cloth.

3. The method defined by claim 1 wherein the refractory metal is a foil.

4. The method defined by claim 1 wherein the refractory metal is a wire.

5. The method defined by claim 1 wherein the baffles extend substantially parallel to the direction of flow of a stream of gas entering the chamber and on opposite sides of the metal on the conveyor belt.

References Cited

UNITED STATES PATENTS

2,461,019	2/1949	Alexander	23—191
2,750,268	6/1956	Erasmus et al.	23—191
2,784,639	3/1957	Keenan et al.	148—166

OSCAR R. VERTIZ, *Primary Examiner.*

H. S. MILLER, *Assistant Examiner.*