Dec. 13, 1949 R. F. RENNIE 2,491,210

TUBE FURNACE FOR PRODUCING METAL

Original Filed Jan. 7, 1943 2 Sheets-Sheet 1

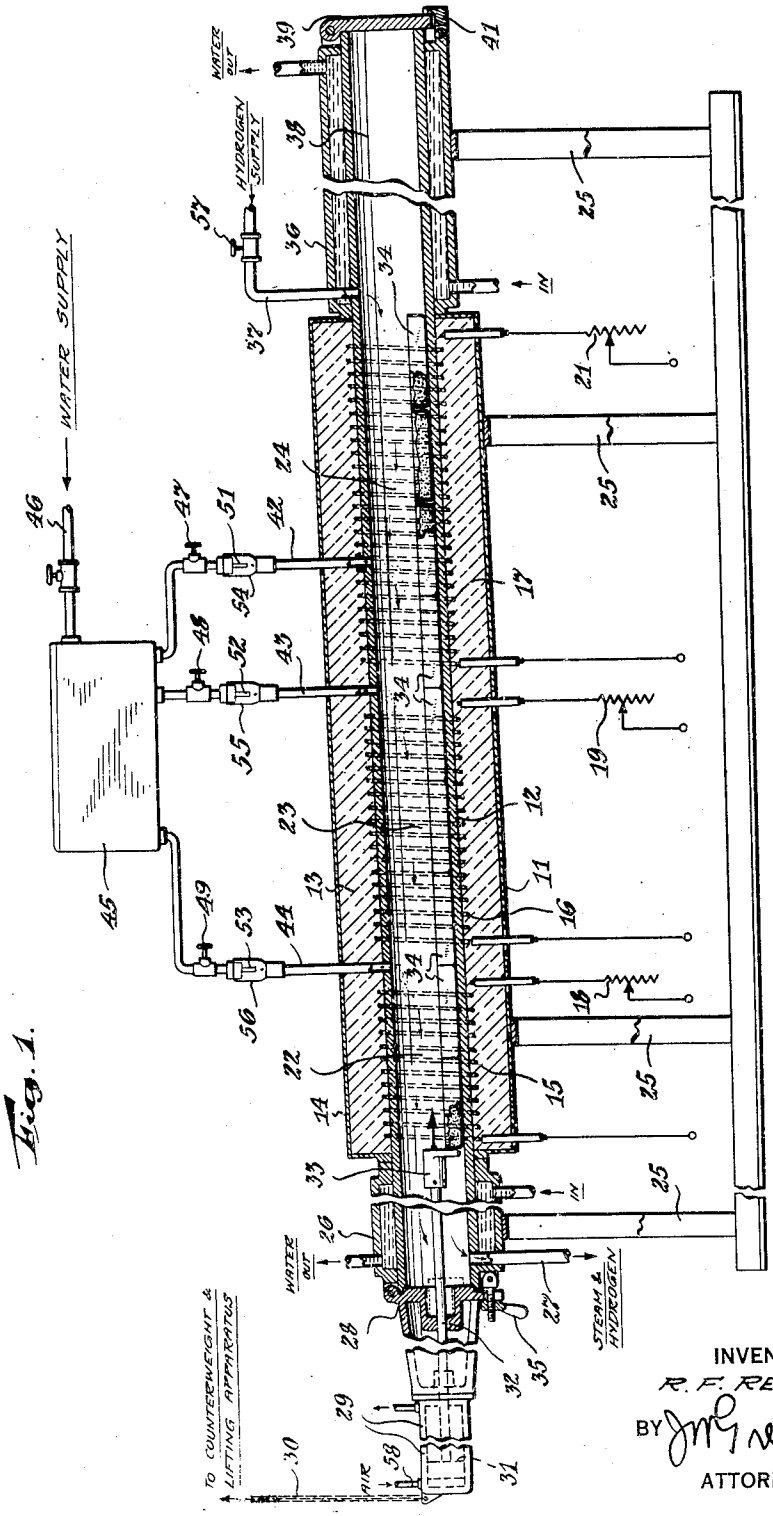

Fig. 1.

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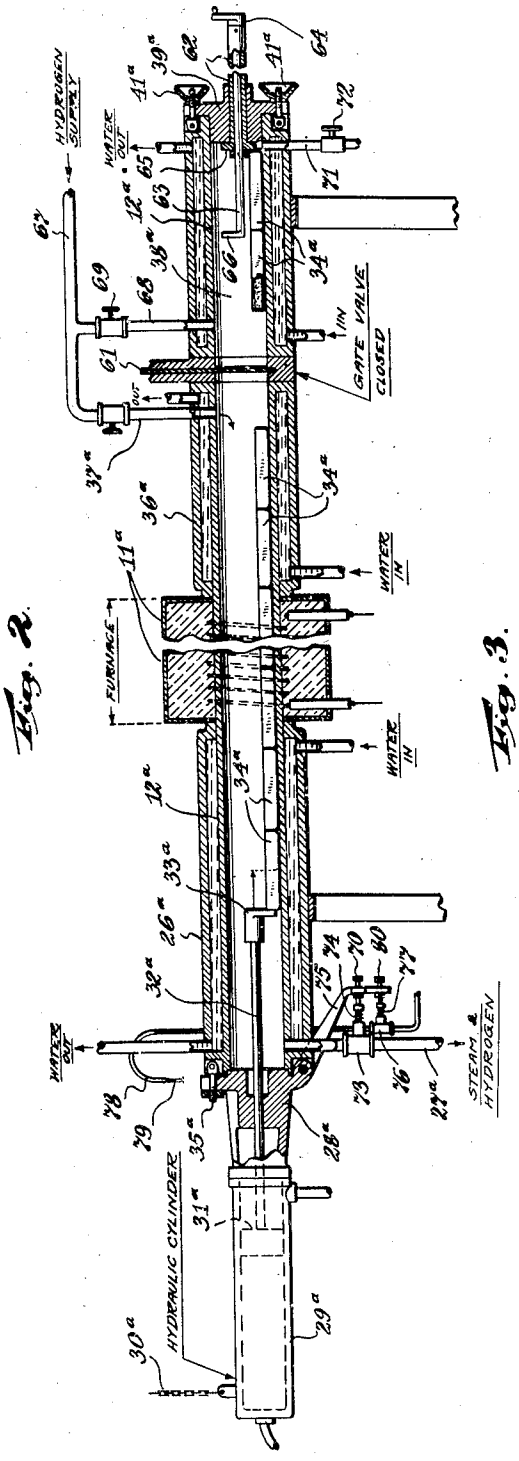

Fig. 2.

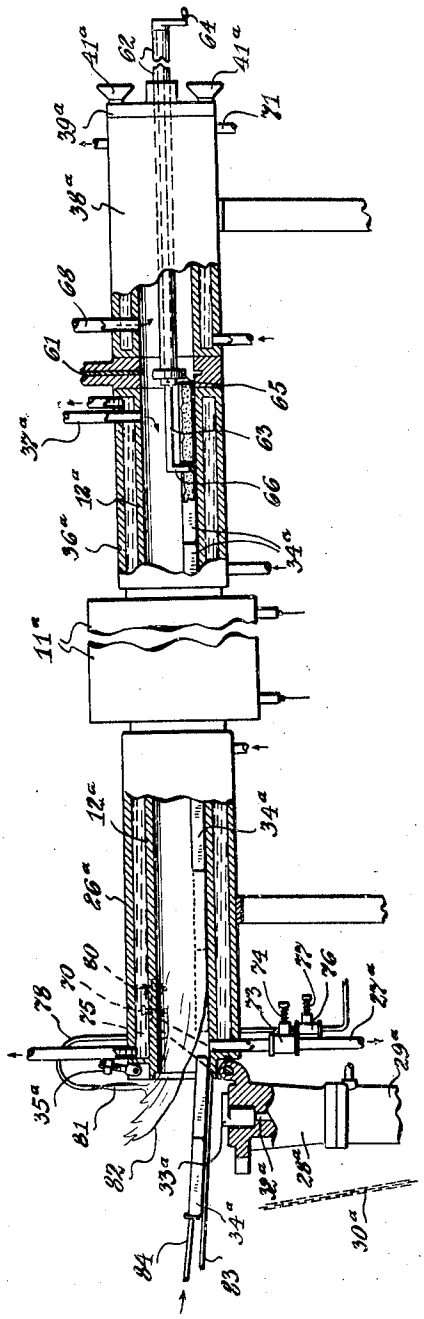

Fig. 3.

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TUBE FURNACE FOR PRODUCING METAL

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Original application January 7, 1943, Serial No. 471,604. Divided and this application November 24, 1945, Serial No. 630,669

4 Claims. (Cl. 13—31)

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This application is a division of my application, Ser. No. 471,604, filed January 7, 1943, now Patent No. 2,402,084, dated June 11, 1946, on Continuous reduction of molybdenum compounds.

This invention relates to the manufacture of molybdenum, and more particularly to a furnace adapted for continuously reducing compounds of molybdenum, such as the trioxide and ammonium molybdate, for that purpose.

The principal object of my invention, generally considered, is in shortening and otherwise improving on the manufacture of molybdenum, starting with a reducible compound, avoiding slow reduction due to keeping the reaction temperature low, and continuously moving the compound through the furnace in a direction opposite to that of the reducing gas.

Another object of my invention is the reduction of molybdenum trioxide, or other reducible compound, to molybdenum, while continuously moving the same in a direction opposite to the flow of the reducing gas.

A further object of my invention is the reduction of a molybdenum compound to molybdenum, by moving it in the furnace continuously through heat zones of increasing temperatures, while passing reducing gas through said furnace in a direction opposite to that of said movement, at the same time stepwise increasing by effective concentration the strength of said reducing gas, to improve the quality of the metal produced and in order to avoid a runaway reaction.

Other objects and advantages of the invention, relating to the particular features will become apparent as the description proceeds.

Referring to the drawing:

Figure 1 is a vertical longitudinal sectional view, with parts in elevation and parts shown diagrammatically, of a furnace and associated apparatus for reducing molybdenum compounds to molybdenum.

Figure 2 is a vertical, longitudinal, sectional view, with parts in elevation and parts shown diagrammatically, of another embodiment of a furnace and associated apparatus for practicing my invention.

Figure 3 is a view similar to Fig. 2, except a furnace part is shown fragmentarily in elevation, and the loading end of the furnace is open while the unloading mechanism is shown in engagement with boats for the purpose of removing them from the furnace.

In my copending application, Serial No. 413,118, filed October 1, 1941, now Patent No. 2,385,843, dated October 2, 1945, I have disclosed a method

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of reducing ammonium molybdate to molybdenum, making use of some of the ammonia generated during the breaking down of the molybdate for reduction purposes, and diluting the hydrogen used in the main reducing action with steam in order to slow down the reaction where necessary and avoid the formation of imperfect metal. This process is an improvement over that previously employed, but is not continuous in that the molybdate is introduced into the furnace and the reducing atmosphere and temperature varied as desired until it is changed to molybdenum, whereupon it is withdrawn.

In my copending application, Serial No. 458,106, filed September 12, 1942, now Patent No. 2,398,114, dated April 9, 1946, I have disclosed a method of reducing molybdenum trioxide to molybdenum, which is similar to that of reducing ammonium molybdate to molybdenum, as disclosed in my application above-mentioned, except that the material is preferably granulated before reduction and I suggested using reducing agents other than hydrogen, it of course being understood that in the reduction of the trioxide there is no ammonia inherently available for reducing purposes.

The present invention involves a furnace especially adapted for practicing an improvement over the above-mentioned processes for stationary reduction of molybdenum compounds by various reducing gases, in that I propose to move the charge to be reduced forward at constant speed into zones of increasing temperature and in a direction opposite to that of the flow of the reducing gas, whereby said gas may be introduced when in its most concentrated or highly reducing condition, and reduced in strength, not only by the steam evolved during the reduction process, but also by the addition of desired amounts of steam along the length of the furnace, thereby avoiding a runaway reaction at the beginning of the reduction process, and improving the quality of the metal which is produced.

Since the time-temperature schedules for such a reduction have been worked out for stationary reductions, as described in the aforementioned pending applications, I have correspondingly arranged the speed with which the charge moves forward and the length of the different temperature zones so as to substantially conform with said schedules, the difference being necessitated by the fact that the control is by the strength of the reducing agent, temperature, length of heating zones, and the speed of movement of the charge therethrough, rather than by varying the flow of hydrogen or other reducing gas and the

amount of diluting material during an increase in temperature of the reduction furnace.

Before this improvement was introduced, there was some difficulty when one tried to decide what flow of hydrogen, or other reducing gas, to use. If the reduction tube was fed with the amount of hydrogen that is needed in the end zone, it would cause a too violent reaction in the zones of lower temperature, or those near where the reaction is beginning. If the furnace was fed with the amount of hydrogen that is wanted at the beginning of the reduction process, the end zone would have to be made impractically long to give complete reduction.

For this reason, continuous processes for reduction of molybdenum compounds up until now have been split into two parts, the end point of the first part being molybdenum dioxide, or a mixture of molybdenum oxide and molybdenum trioxide.

This invention, therefore, supplies a practical solution for a one step reduction of molybdenum compounds to molybdenum by a continuous process. I propose to feed the reduction tube with the hydrogen, or other reducing gas, necessary for speedy complete reduction in the end zone, and at different points admit controlled amounts of steam, or other diluting agent, into the reduction tube to slow down the reaction where necessary and prevent the formation of imperfect metal.

Referring now to the drawing in detail, like parts being designated by like reference characters, and first considering the embodiment of my invention illustrated in Fig. 1, there is shown a furnace 11 consisting of a preferably slightly inclined reduction tube 12, which may be of about 4'' internal diameter and formed of relatively refractory material, such as nichrome. This tube may be covered with suitable insulating material 13, in turn enclosed in a sheet metal envelope 14 and heated in any desired manner, as by means of resistance wires 15, 16, and 17, respectively, controlled by rheostats 18, 19 and 21 to provide three heating zones, respectively designated as 22, 23 and 24.

The windings, insulation, and other characteristics of the furnace are such that the heating zone 22 may be maintained at about 400° C., the zone 23 at about 630° C., and the zone 24 at about 1075° C. The furnace and accessories are desirably held in position as by means of supports 25. The left hand end of the furnace has a section desirably cooled by a water jacket 26 and provided with an outlet pipe 27 for the excess hydrogen, steam and/or ammonia, or other reagent used during the process. It is closed by a hinged door or cap 28, desirably including power means for pushing or otherwise moving the molybdenum compound through the furnace, such as an air or water cylinder 29 and piston 31 for operating a rod 32 and associated pusher element 33. This or other suitable means may be used for moving the containers on boats 34, of the molybdenum compound to be reduced, at uniform speed from the left hand or inlet end of the furnace to the right hand or outlet end. The door or cap 28 may be secured in place by locking means 35, and provided with a chain 30 to a counterweight and lifting apparatus (not shown).

The outlet end of the furnace is provided with a section cooled by a water jacket or like means 36 and provided with a pipe 37 for introducing a supply of hydrogen or other reducing gas. The

extreme end of the cooling section 38 of the tube 12 is closed by a hinged lid or door 39, provided with a suitable latch or locking device 41. Means are provided for introducing desired amounts of water, or other diluting agent, along the length of the tube 12, said means in the present embodiment comprising pipes 42, 43 and 44. Water for these pipes is supplied from a reservoir 45 kept in the desired level as by means of a float valve (not shown) in the water supply pipe 46. The flow of the water from the reservoir to the pipes 42, 43 and 44 is controlled by valves 47, 48 and 49, respectively, admitting water through gaged capillary tubes 51, 52 and 53 and transparent connections 54, 55 and 56, permitting observation of the flow of water.

The hydrogen or other reducing gas supplied passes to the reduction tube at a desirably continuous rate being, however, naturally steadily attenuated during the reaction process by steam and/or other reaction product, with the excess withdrawn from pipe 27 for reclamation after the condensation of any steam therefrom.

I will now describe a preferred reduction schedule of molybdenum trioxide to molybdenum, preferably using hydrogen on granulated material, the manufacture of which has been described in my Patent No. 2,398,114, previously referred to, although I do not wish to be limited to the use of such material, as ammonium molybdate and other reducible molybdenum compounds may be handled in a similar manner. Instead of hydrogen, mixtures thereof such as "Endogas" (which is mainly a mixture of hydrogen and carbon monoxide, diluted with nitrogen) and water gas, and other reducing agents such as carbon monoxide, ammonia, and reducing mixtures, as referred to in said application, Serial No. 458,106, may be employed. It will also be understood that other diluting agents such as nitrogen and carbon dioxide, as referred to in said application, may be employed instead of, or admixed with, steam or with each other. The schedule disclosed is merely illustrative and changes may be made within the broad scope of my invention.

The preferably granulated molybdenum trioxide (MoO_3) is placed in boats 34, desirably formed of refractory metal such as nickel, preferably about 2 kilograms per boat, the material being spread out in the boats to expose as much surface as possible.

The loaded boats may be first introduced into the cool or left hand end portion of the tube 12, after opening the cap or door 28, a sufficient number of boats being placed in front of the pusher element 33 so that the process may be continuous for a desired number of hours without shutting off the flow of hydrogen, or other reducing gas, and replenishing the supply of material to be reduced. After insuring that both doors 28 and 39 are closed and that cooling water is circulating through the water jackets, the hydrogen supply is turned on, as by opening the valve 57, to flush out the air in the tube 12 in order to insure that no explosion will occur when the furnace is brought to a higher temperature.

The electric current is then turned on to the resistance wires 15, 16 and 17, or other heating source applied, until the zones of the furnace reach the desired temperatures, as may be indicated by suitable pyrometers (not shown). That is, the temperature in the zone 22 controlled by wire 15 is desirably 400° C., that in zone 23 controlled by wire 16 is desirably 630° C., and that in zone 24 controlled by wire 17 is de-

sirably 1075° C. The flow of water to the pipes 42, 43 and 44 is regulated so that we desirably get about 3 cc. per minute from the pipe 42, about 9 cc. per minute from the pipe 34, and about 3 cc. per minute from the pipe 44.

The purpose is to admit enough water by pipe 43 to make the reaction to molybdenum dioxide, or intermediate reduction product, to come to a standstill, with approximately 100% of that product at the point of admission of pipe 43. Enough water is to be admitted by pipe 44 to slow the reaction from the molybdenum trioxide, or starting product, sufficiently to prevent overheating and premature formation of imperfect metal. Compared with the stationary reduction described in the applications referred to, more than proportionate amounts of steam must be added because at the point of entry of pipe 43 there will be about 100% excess of hydrogen, and at the point of entry of pipe 44 there will be about 300% excess of hydrogen. This continued addition of steam during the process of reduction desirably coarsens the metal powder produced. This explains the reason for the steam inlet pipe 42, which is not to control the speed of reduction, but to control particle size of reduced metal. In certain cases, however, it may not be necessary to add any water by this pipe 42, or the proportion of water at this point may be varied, depending on the progress of the reduction as determined by experience.

At the same time air is admitted to the end pipe 58, as by means of a suitable control valve (not shown), to cause the pusher element 33 to start uniform movement of the boats 34 through the various zones of the furnace at a rate of speed calculated to leave said boats in zone 22 for about one hour, in zone 23 for about 2¼ hours, and in zone 24 for about 3½ hours. The lengths of said zones are thus made proportionate to the times in which the boats are to remain therein, that is, in the ratio of 1:2¼:3½.

The operation, therefore, starts at about 400° C. with the hydrogen or other reducing gas diluted with a maximum amount of steam, or other diluting agent, not only on account of the introduction of water, but also because of the formation of water by reaction of hydrogen with the oxygen of the molybdenum trioxide, or other oxygen compound, as said agent passes along the reducing tube from right to left. This reducing action by the hydrogen, or other reducing gas, starts the reduction of molybdenum trioxide, or other compound, toward a lower oxidation product, such as the dioxide, avoiding by dilution of a runaway reaction at undesired high temperatures and the production of imperfect metal.

Finally the boats successively reach the next zone where they are heated to a temperature of about 630° C. in a reducing atmosphere more concentrated than that in the zone 22, because there is not only less water admitted in this zone, but there has been less impoverishment of the reducing gas. In this second zone the reduction to molybdenum dioxide is substantially completed so that upon reaching the zone 24, of the higher temperature of about 1075° C., the still more concentrated reducing atmosphere may be safely employed without danger of a runaway reaction or the development of imperfect metal.

It will, of course, be understood that the continuous time of any process, prior to removal of the reduced metal and re-charging with oxide or other compound depends on the length of the

reduction tube, as in the embodiment described the pusher element 33 can operate only until the charge associated therewith reaches the end of the tube or outlet door 39 thereof. It is, therefore, believed desirable that the inlet end of the furnace, or that cooled by the water jacket 26, be of a length corresponding with the intermediate or heated portion thereof, and that the outlet end, or that cooled by the water jacket 36, be of a corresponding length, so that a charge of boats equal in length to the heated portion of the tube, that is the portion consisting of the zones 22, 23 and 24, may be started in the cool left hand end of the furnace and the operation continued until completed, when the entire charge will have been moved to the outlet end. Thereupon the hydrogen or reducing gas supply may be shut off, the heating current terminated, the flow of water or other diluting agent stopped and, when the furnace is sufficiently cool to avoid undesired oxidation of the reduced metal, the door 39 may then be opened and the charge of metal removed, after which the door 39 may be opened and a new charge of oxide, or other reducible molybdenum compound, introduced and the process repeated.

Referring now to the embodiment of my invention illustrated in Figs. 2 and 3, there is fragmentarily shown a furnace 11a, which may be identical with the furnace 11 of the preceding embodiment insofar as the central or heating section is concerned. However, the left hand or loading end of the inclined reduction tube 12a of the furnace of the present embodiment, has a section that is cooled by water jacket 26a and provided with an outlet pipe 27a for excess hydrogen, steam and/or ammonia or other reagent used during the process, and said section need not be as long as the furnace or heating section for reasons which will be explained.

In the present instance the loading end of the tube 12a is closed by a door or cap 28a, including power means for pushing the molybdenum compound through the furnace, such as, for example, an hydraulic cylinder 29a, piston 31a, operating rod 32a, and associated pusher element 33a. This or other suitable means may be used for moving the containers or boats 34a of the molybdenum compound at uniform speed, from the left hand or inlet end of the furnace to the right hand or outlet end. The door or cap 28a is, in the present instance, hinged at its lower end rather than at its upper end and normally secured in place by locking means 35a. As in the preceding instance, the cylinder 29a is provided with a chain 30a to a counterweight and lowering apparatus (not shown).

The outlet end of the furnace is provided with a section, cooled by water jacket or like means 36a and provided with a pipe 37a for introducing a supply of hydrogen or other reducing gas. The extreme end of the cooling section 38a of the reduction tube 12a is closed by a cap or lid 39a, provided with suitable latch or locking device 41a. The cooling section 38a of the reduction tube 12a is in this instance formed in two sections which may be separated as in Fig. 2, or connected as in Fig. 3, by closing or opening the gate valve 61.

The cap 39a is provided with an aperture containing a sleeve element 62 and hooked rod 63, controlled by a handle 64, so that they are adapted to be reciprocated and turned at will. They may be moved toward the entrance end of the reduction tube when the gate valve 61 is

open, as in Fig. 3, and turned so that the hooked end portion 66 of the rod 63 engages one or more of the boats 34a to pull it, or them, to the right hand position shown in Fig. 2, whereupon the gate valve may be closed, the cap 39a and its associated sleeve and rod removed, and the boats taken out of the furnace. The sleeve 62 is desirably provided with a collar or flange 65 which is adapted to engage the forward or right hand end of a boat 34a to tell the operator when to turn the handle 64 so that the hooked end portion 66 thereof will connect with the boat or boats 34a nearest the exit end of the furnace.

The hydrogen supply pipe 67 is desirably provided with a branch 68 controlled by a valve 69 so that the extreme right hand section of the reduction tube, or that beyond the gate valve 61, may, prior to opening said valve to resume the reducing operation, be flushed out with hydrogen so that when said gate valve is opened an explosive mixture will not be formed. During the flushing operation the air is exhausted through pipe 71 controlled by valve 72.

The operation of the embodiment of my invention illustrated in Figs. 2 and 3 may be as follows:

The loaded boats of the reducible compound, such as the granulated trioxide, may be first introduced into the cool or left hand end portion of the tube 12a after dropping the cap or door 28a. Any convenient number of boats are placed in front of the pusher element 33a. When the door 28a is open, the valve 73 in the hydrogen exhaust pipe 27a is closed as by releasing the spring actuated stem 74 thereof by swinging the adjustable pusher element 70 of the operating arm 75 from engagement therewith. The arm 75 is integral with or connected to the door 28a so as to swing therewith.

At the same time the valve 76 is opened, as by release of its spring actuated stem 77 by disengagement of the arm-carried adjustable pusher element 80, to increase the supply of gas to the pipe 78 to change the pilot light 79 issuing therefrom to a relatively long flame 81 and thereby ignite the issuing hydrogen, or other reducing gas 82, and prevent the formation of an explosive mixture.

When the furnace is open, as represented in Fig. 3, then the charge of boats 34a may be introduced, as by pushing them in along a loading plate 83 by means of a pusher element 84, after which the door 28a is closed as in Fig. 2, automatically reducing the flame 81 to the pilot light 79 and opening the reducing gas exhaust pipe valve 73 by bringing the operating arm 75 into engagement therewith.

The hydrogen, or reducing gas supply is then turned on, the furnace brought up to temperature, and the reducing action started as described in connection with the embodiment of Fig. 1. The hydraulic cylinder or other operating means pushes the boats 34a a desired distance into the furnace, whereupon the pusher element 33a may be withdrawn, the filling end of the furnace opened, and some more boats placed therein, as illustrated in Fig. 3.

This pushing and withdrawing operation is repeated until it is estimated that the boats at the head or right hand end of the line are coming close to the gate valve 61. Said gate valve 61 is then opened, the hooked rod 63 moved from the position shown in Fig. 2 to that shown in Fig. 3 and turned to engage one or more of the boats 34a and pull them to the extreme right

hand position shown in Fig. 2. The gate valve 61 is then closed, the exit cap 39a and its hooked rod 63 removed therefrom and the captured boats taken out of the furnace. The cap 39a and rod 63 are then reapplied to the furnace as in Fig. 2, the outer section or that to the right of the valve 61 flushed out with hydrogen, the valves 69 and 72 closed, the gate valve 61 opened.

It will be understood that the reducing operation may be continued uninterruptedly during the operation of the loading or unloading of the furnace. The short stoppage time taken for loading is allowed for as part of the reduction time, the time taken for unloading, however, not affecting the reduction time because during the unloading operation the piston 31a may operate and continue to push the boats from left to right in the reduction tube.

It will be understood that the description of the apparatus of Fig. 2 is to be supplemented by the description of the apparatus of Fig. 1, insofar as the details of the furnace or heating portion of the apparatus is concerned. The essential difference between the two embodiments is that in connection with the second the loading piston will periodically move back to accommodate charges, that is, move at a substantially continuous and uniform rate punctuated only by the brief loading intervals, and the reduced metal will be withdrawn without stopping the furnace, while in the first embodiment the charge is started at the loading end and pushed on through to the unloading end without opening the furnace or stopping the movement of the boats in any manner.

Although preferred embodiments of my invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

I claim:

1. Apparatus for manufacturing molybdenum comprising a furnace consisting of an inner reduction tube of refractory material, a plurality of heating coils of resistance wire surrounding said tube and independently controlled, insulating material enclosing said coils and tube, one of said coils serving to heat an intermediate portion of said tube and coils at opposite ends thereof serving, respectively, to heat portions of said tube toward its opposite ends, whereby said tube may be heated to different temperatures along its length, a door closing the loading end of said tube, a rod reciprocable in said door, a fluid-pressure cylinder connected to said door, a piston in said cylinder and connected to said rod for pushing containers of molybdenum oxide along said reduction tube, a gate valve which when closed divides the other end portion of said tube into two parts, a door for the unloading end of said tube, a hooked rod slidable in said door, a handle on the outer end of said rod to pull containers of reduced metal from one side of said valve to the other, pipe connections for introducing gas to said tube portion at both sides of said valve, and pipe connections adjacent the ends of said tube for exhausting said gas, so that when said valve is closed, said tube between said gate valve and unloading end door may be flushed out by said gas, whereby a periodically replenished charge of molybdenum oxide may be substantially continuously moved along said reduction tube and the reduced metal withdrawn at desired time intervals without stopping the reducing operation.

2. Apparatus as defined in claim 1 in which a water jacket surrounds a portion of said reduction

tube beyond one of said end coils adjacent the loading end of said tube, and another water jacket surrounds the other end portion of said tube beyond said other end coil adjacent the unloading end of said tube.

3. Apparatus for manufacturing molybdenum comprising a furnace consisting of an inner reduction tube of refractory material, a plurality of heating coils of resistance wire surrounding said tube and independently controlled, insulating material enclosing said coils and tube, one of said coils serving to heat an intermediate portion of said tube and coils at opposite ends thereof serving, respectively, to heat portions of said tube toward its opposite ends, whereby said tube may be heated to different temperatures along its length, a fluid-pressure cylinder connected to said door, a piston in said cylinder and connected to said rod for pushing containers of molybdenum oxide along said reduction tube, a door for the unloading end of said tube, a pipe connection for introducing combustible gas to said tube, another pipe connection for exhausting the gas from said tube, a valve in said other pipe connection, a pipe from a supply of combustible gas for normally providing a pilot light near the loading end of said tube, a normally only partly open valve in said pipe, and an arm connected to swing with the door closing the loading end of said tube and so related to said valves that it closes the valve in the exhausting pipe connection and further opens the valve in the pilot light pipe, as the door is opened, so as to then allow all of the gas in the tube to flow out of the loading end thereof and be met by a relatively-long flame, instead of a mere pilot light, to thereby ignite the gas from said tube and prevent the formation of an explosive mixture.

4. Apparatus as defined in claim 3 in which a water jacket surrounds a portion of said tube beyond one of said end coils adjacent the loading end of said tube and another water jacket surrounds the other end portion of said tube beyond said other end coil adjacent the unloading end of said tube.

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