United States Patent

Schroder

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[54] **HEATER SYSTEM**

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[52] **U.S. Cl.**..**126/263**

[51] **Int. Cl.**..**F24j 1/00**

[58] **Field of Search**..............................126/263, 204; 165/46

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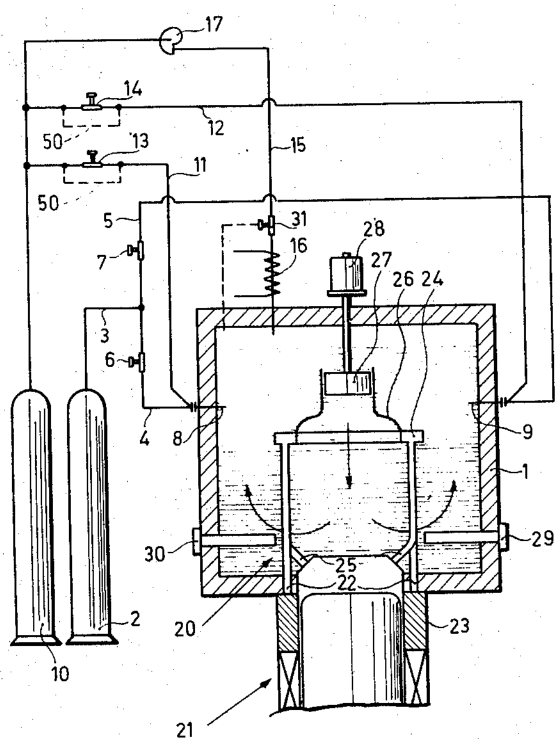
[57] **ABSTRACT**

A heater system comprising a reaction vessel containing a mixture of metals which is melted during operation, an oxidant container, at least one duct with outlet member for communicating the oxidant to the reaction vessel for an exothermic reaction therein with the metal mixture, and a container having an inert gas which communicates via a regulating valve with the duct between the oxidant container and the reaction vessel; the outlet member is readily cooled and manufactured from a material which is not or substantially not wetted by the liquid in the reaction vessel.

12 Claims, 8 Drawing Figures



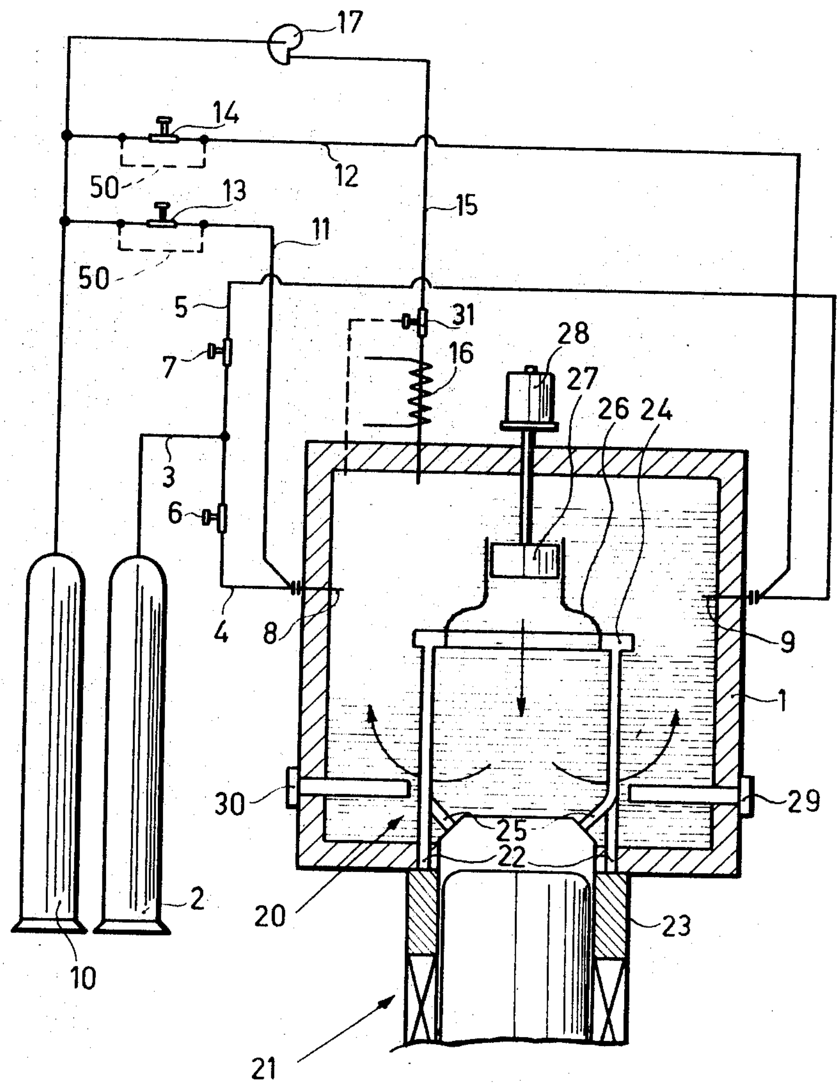


fig.1

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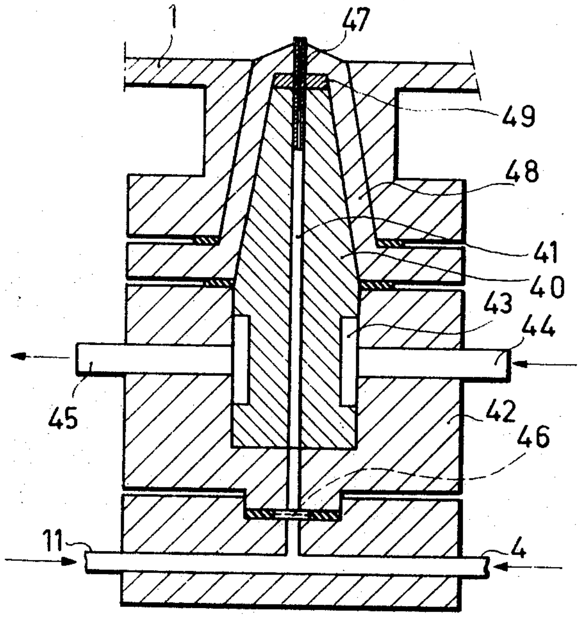

fig.2

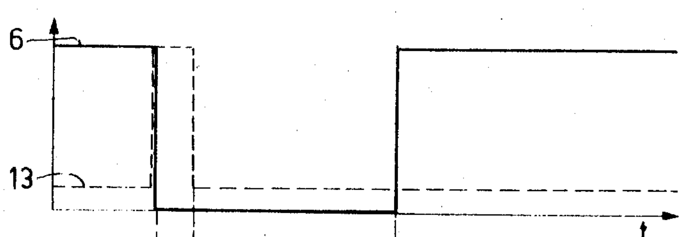

fig.3a

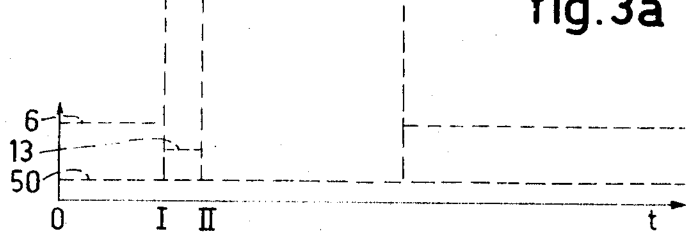

fig.3b

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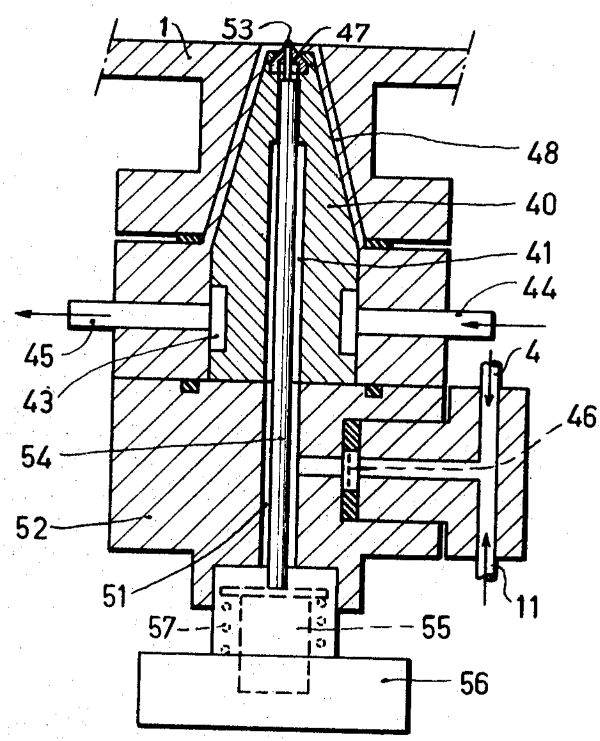

fig. 4

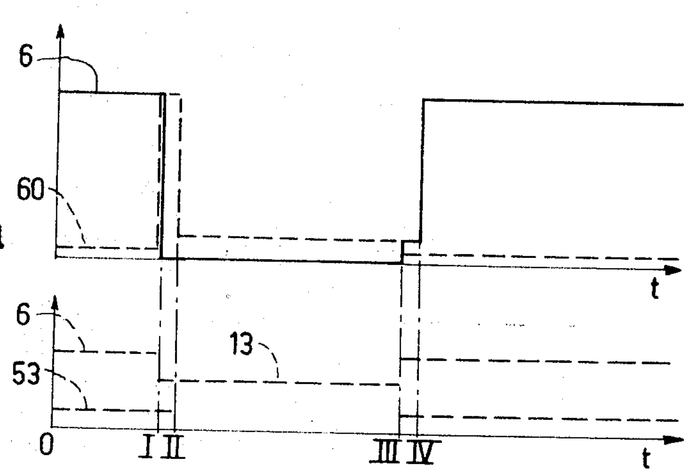

fig.5a

fig.5b

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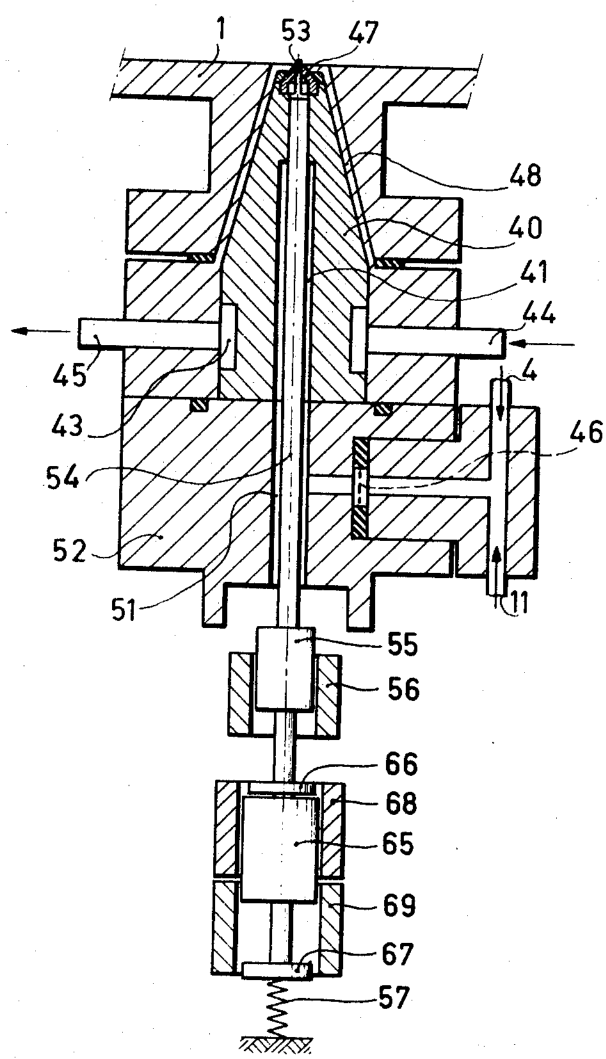

fig. 6

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HEATER SYSTEM

The invention relates to a heater system, particularly for the supply of heat to a heat exchanger in which a medium flows. The system comprises a reaction vessel containing a metal or a mixture of metals which is liquid at the operating temperature, a first container containing an oxidizing agent which is capable of reacting chemically with the liquid in the reaction vessel while evolving heat in such manner that the reaction products are solid and/or liquid at the temperature and pressure prevailing in the reaction vessel. This vessel communicates through a duct including a regulating valve, with at least one supply duct communicating with the reaction vessel; the system furthermore comprises a second container containing a gas which is chemically inert with the liquid in the reaction vessel and with the oxidant, the second container communicating also with the supply duct through a duct comprising a regulating valve.

Heater systems of the type to which the present invention relates are known and have the advantage that they can supply heat independently of the surroundings in which they are arranged. In other words, said heater systems supply heat without consuming air of combustion and without giving off gases of combustion. So they are excellently suitable for use in those places where pollution of air by gases of combustion is sought to be avoided or is prohibited.

Such heater systems can be used in all devices in which heat is required, and may serve, for example, for supplying heat to engines in which a working medium traverses a thermodynamic cycle between an expansion space which is at a high temperature and a compression space which is at a low temperature examples being gas turbine systems and hot gas engines. The supply of heat from the heater system to the engine or turbine may take place by conveying liquid in the reaction vessel to the heater which usually is a pipe heater through which the working medium flows. If desirable, the heat transfer from the reaction vessel to the heater may also take place by means of a heat transporting medium, for example, liquid NaK, which circulates in a system of ducts which at one end is in heat exchanging relationship with the reaction vessel and at the other end with the heater.

During operation of the above type system a temperature of, for example, 800° C prevails in the reaction vessel. The metal or mixture of metals in the reaction vessel may be constituted by one or more of the metals Li, Ca, Na, K, Mg, Al and/or one or more of the rare earth metals. These metals, and particularly combinations thereof, have the advantage of a comparatively low melting temperature and a large evolution of heat per unit by volume.

An oxidant such as a halogen or a halogen compound, particularly fluorine or a fluorine compound may be used. The oxidant is supplied to the reaction vessel in dosed quantities in which the oxidant reacts chemically, while evolving heat, with the liquid metal. In this case salts are formed which are solid and/or liquid.

A difficulty is that at the temperature of approximately 800° C prevailing during operation in the reaction vessel, all the construction materials to be considered for the reaction vessel and the supply ducts, react with the oxidant which results in disturbances.

It is the object of the invention to provide a solution to this problem, and the invention is based on the recognition of the fact that (a) contact between oxidant and vessel walls is to be avoided as much as possible, while (b) those parts such as the supply ducts which necessarily have to contact the oxidant are kept at such a low temperature that no reaction occurs between the oxidant, and said parts.

To achieve the above object, the heater system according to the invention has the end of the supply duct facing the reaction vessel communicating with one end of a duct in a cooled, readily heat-conducting block of material; the other end of said duct comprises an outlet member which is secured in said duct and makes a good thermal contact with the block of said material. This member is manufactured from or provided with a superficial layer of a material which is not or substantially not wetted by the liquid in the reaction vessel; the block of material is incorporated in an aperture of the wall of the reaction vessel with the interposition of a heat insulator. This passage of the outlet member and the pressure of the oxidant and the gas in the supply duct are furthermore chosen such that the rate of flow of the oxidant or the gas in the outlet member is larger than the reaction speed of the oxidant with the metal or mixture of metals in the reaction vessel. With this arrangement the metal cannot penetrate into the outlet member.

Due to this construction of the outlet member, the temperature thereof is kept low (a) by the cooling, which may be water cooling, and (b) by the rapid flow of the oxidant and the gas, which also provides cooling so that the oxidant does not react with the material thereof. The rapid flow of the oxidant and the gas has the further result that the oxidant is injected in the metal melt, so that it substantially does not contact the hot walls of the reaction vessel. Furthermore, the fast-flowing mixture of oxidant and inert gas ensures that the metal cannot penetrate into the supply duct where it would solidify and thus clog the passage.

By manufacturing the outlet member from a material which is substantially not wetted by the liquid in the reaction vessel, there is prevention of the liquid, in spite of the fast flow of gas, from creeping along the walls into the outlet member, solidifying there and narrowing the passage. In this manner an extremely reliable heater system is obtained.

According to a further favorable embodiment of the heater system in which the reaction vessel contains mainly Li and Ca or salts thereof and the first container contains fluorine or a fluorine compound such as SF_6, the outlet member is manufactured from or provided with a superficial layer of one of the metals tungsten, molybdenum or tantalum or one or more of the carbides or borides of said metals. These materials have the property that they are substantially not wetted by liquid Li and Ca and their salts.

In order to prevent the narrow outlet member from getting clogged by contaminations, if any, in the supplied current of gas, a filter element such as a gauze, is arranged in the duct in the block of material or in the supply duct; this gauze has duct passages and mesh widths, respectively, of a smaller dimension than the passage of the outlet member.

A further embodiment of the heater system according tot the invention is characterized in that a regulating device is present with which the regulating valves in the ducts of the first and the second container communicating with each of the supply ducts can be controlled in such manner that upon closing the regulating valve in the duct communicating with the first container, the regulating valve in the duct communicating with the second container is opened for a moment and is then immediately closed, a bypass with a narrow passage being arranged across said latter valve so that a constant flow of inert gas flows from the second container to the reaction vessel.

So in this embodiment a small flow of an inert gas, supplied via the bypass, flows with the flow of oxidant.

Upon closing the oxidant suppletion valve, the rate of flow in the outlet member suddenly becomes smaller, and the danger exists that the reaction speed of the metal with the oxidant becomes larger than the outflow rate, which would mean that the metal enters the outlet member and the supply duct. In order to prevent this, the valve in the inert gas supply duct is opened for a moment when the oxidant suppletion valve is closed. As a result of this a large flow of inert gas will be supplied for a moment, which forces the oxidant at a large speed out of the supply duct and the outlet member. The valve in the inert gas supply duct is then closed again. The remaining flow of inert gas is now sufficient to prevent penetration of metal. Now only a comparatively small quantity of inert gas is supplied to the reaction vessel, the advantage of which is that the quantity of inert gas to be removed therefrom is also small, so that said circulation by pumping of inert gas can take place with a comparatively small effort.

In another embodiment, a needle valve is present, which preferably can be operated electromagnetically and which can fully or partly close the passage of the outlet member. In this embodiment the position of the needle valve can always be adapted to the supplied flow of oxidant, so that always a high speed occurs in the passage of the valve and hence no metal can penetrate. Furthermore, it is possible to close the passage entirely when no oxidant is supplied, so that in this case also no inert gas need be circulated by pumping.

Fully closing the flow aperture by means of the needle valve presents difficulties in circumstances because, for example, the valve remains adhered on the seating. In order to prevent this, the valve is not fully closed and, according to the invention, a regulating device is present which controls the regulating valves in the ducts between the supply duct and the first and second containers, respectively, in opposite phases. Upon closing the oxidant supply valve, the needle valve moves to its slightly open position, so that, when the supply valve for inert gas is simultaneously opened, only a small quantity of inert gas will flow to the reaction vessel. So in this embodiment it is again prevented that a large flow of inert medium has to be circulated by pumping.

According to a further embodiment, the movements of the needle valve lag slightly with respect to the movements of the regulating valve in the ducts communicating with the first container. In this manner it is achieved that upon closing the oxidant supply valve and opening the inert gas supply valve, a large flow of inert gas flows through the outlet member for a moment, so that the oxidant is driven out. The flow of inert gas then becomes much smaller.

Although it is possible when using a needle valve for opening and closing the passage of the outlet member to control the valve in the supply ducts for oxidant and inert gas in opposite phases, so that during operation only oxidant is supplied to the reaction vessel, it has been found of advantage to provide a bypass with a narrow passage across the regulating valve in the inert gas duct communicating with the second container. In this manner a small flow of inert gas will always flow with the flow of oxidant. This has the surprising result that less noise occurs during the reaction in the reaction vessel.

It has been found that in circumstances it may occur that when the valve is closed it adheres to the seating, so that opening becomes difficult, while, when the valve is opened, a small quantity of metal or salt sometimes deposits on the valve seating which can be removed by impacting the valve forcibly on the seating. Both for detaching an adhered valve and for pushing away deposited metal or salt parts, a comparatively large force is required which can normally not be supplied by the electromagnet which controls the valve. In order to avoid this problem, a further favorable embodiment comprises, in addition to the armature of the operating electromagnet, a further armature which is slidably provided on the valve stem between two stop members which are provided on the valve stem, two electromagnets being present, one of which is capable of pulling said slidable armature against one stop member and the other against the other stop member. The slidable armature will hit the stop members with a given shock, so that the valve also hits the seating with a shock.

In order that the invention may be readily carried into effect, it will now be described in greater detail, by way of example, with reference to the accompanying drawings, in which

FIG. 1 diagrammatically shows, not to scale a construction of a heater system.

FIG. 2 diagrammatically shows an outlet member.

FIG. 3 is a diagram for regulating the gas flow through the outlet member shown in FIG. 2.

FIG. 4 shows on an enlarged scale another embodiment of an outlet member,

FIG. 5 shows a diagram for regulating the gas flow through the outlet member shown in FIG. 4,

FIG. 6 is a further embodiment of the outlet member shown in FIG. 4.

Reference numeral **1** in FIG. **1** denotes a reaction vessel containing a metal mixture of mainly Li and Ca which is melted at the operating temperature of approximately 800° C. Reference numeral **2** is a first container containing a fluorine compound as an oxidant which communicates via duct **3** with a number of supply ducts, of which, **4** and **5**, are shown, and further includes regulating valves **6** and **7**, and outlet members **8** and **9**, respectively, on its side facing the reaction vessel.

The heater system furthermore comprises a second container **10** containing argon which communicates, via ducts **11** and **12** including regulating valves **13** and **14**, with the supply ducts **4** and **5**. An argon outlet duct **15** furthermore communicates with the reaction vessel **1** through a cooler **16**, from a compressor **17**, the compression side of which communicates with the container **10**.

The heat evolved in the reaction vessel **1** is transferred to a heater **20** of a hot-gas engine **21** shown only partly and arranged in said vessel. The heater **20** consists of a number of pipes **22** which communicate at one end with the regenerator **23** and at the other end with an annular duct **24**, and of a number of pipes **25** which communicate the annular duct **24** with the expansion space. Secured to the annular duct is a guiding plate **26** constructed as a body of revolution in which a pump **27** coupled to an electric motor **28** can rotate. The liquid is circulated by said pump as is denoted by arrows. During the circulation, the liquid passes the pipes **22** and **25**, respectively, arranged in a ring so that a good heat transfer is ensured between the liquid and the pipes.

The operation of this system is as follows. First the metal mass is melted by heating by means of the electric heating device **29** and **30**. By opening the regulating valves **6** and **7**, the fluorine compound is then introduced into the reaction vessel in which said compound reacts chemically with the metal while evolving heat. In order to prevent liquid metal from penetrating into the outlet members **8** and **9** a flow of argon can be conducted along with the fluorine current, continuously or in those periods in which the fluorine current is too low to check said penetration, by opening valves **13** and **14**, so that a sufficient flow rate in the outlet members occur to check penetration of metal. The argon which is conducted along does not react with the metal and is collected in the upper side of the reaction vessel. With the regulating valve **31** arranged in the argon outlet duct **15** the argon pressure is maintained at a given constant value. This pressure also ensures that the pump **27** operates smoothly so that a liquid circulation occurs in the container **1**, and the liquid can supply its heat to the heater pipes **22** and **25**, respectively.

Since the fluorine compound is extremely agressive, and at higher temperatures reacts with all the construction metals to be considered, not only the flow rate in the outlet members **8** and **9** should be sufficiently high to check penetration of liquid, but furthermore the construction of said outlet members should be so that the temperature remains low enough to prevent attack by the fluorine.

FIG. 2 shows an outlet member on an enlarged scale. It comprises a copper block **40** in which a duct **41** is recessed. The block **40** is surrounded by a metal member **42**, with a cooling jacket **43** present between said metal member **42** and the copper block **40**, including a cooling water supply inlet **44** and a cooling water outlet **45**. The duct **41** extends in the metal member **42** and communicates with the supply **4** inlet for the fluorine compound and the supply **11** for argon, respectively. A metal gauze **46** is arranged in the duct **41**. An outlet member **47** made from tungsten is secured in the duct **41** so as to be readily heat conducting. The copper block **40** is secured in an aperture in the wall of the reaction container **1** with the interposition of a stainless steel and hence insulating jacket **48**. Between the end face of the copper block **40** and the stainless steel jacket a thermal insulation layer **49** is provided. The passage of the outlet member **47** and the pressure of the fluorine compound and argon are chosen such that in the outlet member the rate of flow is larger than the reaction speed of the metal with the fluorine compound, and for that reason penetration of the metal will not occur. Furthermore, tungsten can hardly or cannot be wetted by the liquid in the reaction vessel, so that creeping in of metal along the walls of the outlet member is unlikely. The large rate of flow of gas in the outlet member cools this member considerably, so that the temperature will remain lower than the temperature at which the fluorine compound will react with the tungsten. Furthermore, the outlet member is cooled by the water which withdraws heat from the copper block **40** and hence from the outlet member **47** in the cooling jacket **43**. In this manner a reliable outlet member is obtained.

Regulating the fluorine compound and argon flow through the outlet members may occur as is diagrammatically and idealized shown in FIG. 3, for the outlet member **8**. FIGS. *3a* and *3b* show in the horizontal direction the time *t* with lines **6** and **13** of FIG. *3a* showing the value of the fluorine and argon flow, and lines **6, 13** and **50**, in FIG. *3b* showing the opened position of valves **6, 13** and bypass **50**, respectively.

At the instant **0** the valve **13** in the argon supply duct is closed so that only argon can flow through the bypass **50** across the valve **13**. Furthermore, the valve **6** is fully opened so that a large flow of oxidant occurs.

At the instant I the valve **6** is closed and the valve **13** is opened for a moment. The result of this is that the flow of oxidant becomes zero and a large flow of argon is obtained for a moment which rapidly cleans the outlet member. At the instant II the valve **13** is closed again and the remaining small flow of argon through the bypass **50** is sufficient to prevent penetration of metal into the outlet member **47**. In this manner there is a minimum of argon circulated by pumping from the container **10** to the reaction vessel **1** and via compressor **17** and back is sufficient.

FIG. 4 shows another embodiment of the outlet member **8, 9** on an enlarged scale. Those parts which correspond to the parts of the outlet member shown in FIG. 2 are referred to by the same reference numerals. **40** is again a copper block in which a duct **41** is recessed. On its side facing the reaction vessel, an outlet member **47** of tungsten is secured in the duct **41** so as to be readily heat-conducting. The copper block is secured in an aperture in the wall of the reaction vessel **1** with the interposition of a stainless steel jacket **48**. In this jacket are provided an inlet **44** and an outlet **45** for cooling water which communicate with a cooling jacket **43** around the copper block. The duct **41** continues in a duct **51** in a structural component **52**, which duct **51** communicates via a metal gauze **46**, with the supply duct **4** for oxidant and the supply duct **11** for argon. In the outlet member **47** a needle-like valve body **53** is provided which comprises a valve stem **54** which comprises on its other side an armature **55** of an electromagnet **56**. A spring **57** exerts a closing force on the valve stem **54**.

The operation will be explained also with reference to FIGS. *5a* and *5b*. FIG. *5a* shows idealized the value of the oxidant and argon flow as a function of time, while FIG. *5b* shows the positions of the valves **6** and **13** and of the needle valve **53**, associated with the said flows.

In the period O–I the valve **6** and the needle valve **53** are both open, so that in this period a large flow of oxygen (denoted by line **6** in FIG. *5a*) flows through the outlet member **47**. Simultaneously with the flow of oxidant, a small flow of argon flows via the bypass **50** through the outlet member. The passage of said outlet member and the oxidant and argon pressure are chosen to be so that the rate of flow is sufficiently large to check penetration of liquid. Furthermore the outlet member is sufficiently cooled to maintain a temperature at which the oxidant does not react with tungsten. At the instant I the valve **6** is closed and the valve **13** is opened. Now a large flow of argon flows to the outlet member thereby rinsing away the oxidant still present. A moment later, at the instant II, the needle valve **53** moves to its closed position, the passage of the outler member being considerably reduced so that only a small quantity of argon flows to the reaction vessel at a high speed. In this manner a comparatively small quantity of circulating argon is sufficient again. At the instant III the valve **6** is opened again and the valve **13** is closed. A moment later, at the instant IV, the needle valve **53** opens again, so that a large flow of oxidant flows to the reaction vessel **1**. The value of the argon flow is denoted in FIG. *5a* by broken lines **60**.

FIG. **6** shows the same outlet member as FIG. **4**, in which a second slidable armature **65** is provided on the valve stem **54** beside the armature **55**. This armature **65** can slide between two stop members **66** and **67**. Furthermore two electromagnets **68** and **69** are present. The operation is as follows: When opening the valve the magnet **56** is energized while simultaneously magnet **69** is also energized, so that the movable armature moves to the stop member **67** and impacts against it with a shock. Due to this shock the valve **53**, also when it is adhered to the seating, will easily be detached after which further opening by the magnet **56** can take place. Upon closing, the magnets **56** and **59** are not energized and the magnet **68** is energized indeed. The spring **57** moves the valve to the seating, in which it obtains an extra shock because the armature **65** impacts against the stop member **66**. Due to this shock, any metal or salt particles deposited on the valve seating will be detached. In this manner a very reliable valve is obtained.

From the above it may be obvious that the invention provides an extremely reliable heater system. It is to be noted that although in the drawing only one example is shown, various other constructions, for example, employing several reaction vessels or several spare containers are possible without essentially departing from the scope of the invention.

What is claimed is:

1. A heating system for providing heat from an exothermic reaction of a first material, namely an oxidizing agent with a second reactant material namely a metal or metal mixture which is liquid at operating temperature, and using a third material, namely gas inert to both the first and second materials, comprising

a. a reaction vessel for containing said reactant material and exothermic reaction,

b. a first container for said oxidizing agent,

c. a first supply duct for conveying said agent,

d. a second container for said inert gas,

e. a second supply duct for conveying the inert gas to join said oxidizing agent in the first supply duct,

f. means for regulating the pressures of said materials in said system,

g. connection means for communicating said oxidizing agent and inert gas from the supply duct outlet into the reaction vessel, the connection means including:

(i) a base element made of good heat-conducting material, having mounting surfaces for engaging the reaction vessel, and a passage therethrough with an outlet end for the flow from said first supply duct, this outlet end being substantially non-wettable by the reactant material in the reaction vessel, and (ii) a heat-insulating material interposed between said base element mounting surfaces and the vessel, the diameter of said passage and the pressure of the oxidizing agent and inert gas being selected and regulated by said means for regulating pressures, such that the rate of flow of the oxidizing agent and inert gas in said passage is greater than the reaction speed of the oxidizing agent with the reactant material in the reaction vessel.

2. A system according to claim **1** wherein the non-wettable part of the base element is an outlet member (i) that is secured in good thermal contact with the outlet end of the base element, and (ii) that has a passage through which the base member outlet discharges to the reaction vessel.

3. A system according to claim **1** wherein said base part is copper, the non-wettable part is tungsten, and the heat-insulating material is stainless steel.

4. A system according to claim **1** further comprising a regulating valve associated with each of said first and second supply ducts.

5. A system according to claim **1** wherein the reaction products are solid or liquid or a combination thereof at the temperature and pressure prevailing in the reaction vessel.

6. A system according to claim 1 wherein the reactant material comprises Li and Ca or salts thereof, and the oxidizing agent is fluorine or a fluorine compound such as SF_6, and wherein the base part outlet end is a metal layer such as tungsten, molybdnum or tantalum, or one or more of the carbides or borides of said metals.

7. A system according to claim 1 further comprising in said first supply duct and in said base part passages, a filter element such as a gauze having mesh apertures of smaller cross-sectional dimensions than the passage of the base element.

8. A system according to claim 1 wherein said means for regulating the pressure comprises first and second regulating valves respectively in the first and second ducts, and a bypass duct having a narrow passage in parallel with said second regulating valve for permitting a constant flow of gas from the second container to the reaction vessel.

9. A system according to claim 1 further comprising a needle valve for selectively closing the outlet end of the base element passage, and electromagnetic means for operating said needle valve.

10. A system according to claim 1 wherein said means for regulating pressure comprises regulating valves in said first and second ducts operable in opposite phases, and includes a bypass having a narrow passage arranged in parallel with the valve in the second duct.

11. A system according to claim 9 wherein the regulating means further comprises a regulating valve in the first duct operable to control the needle valve in such manner that the movements of the needle valve lag slightly with respect to those of this regulating valve.

12. A system according to claim 10 wherein the needle valve has a stem and an armature movable on the stem between two stop members, and two electromagnetics, one of which moves said armature in the direction of one stop member, and the other which moves said armature in the direction of the other stop member, whereby the valve stem is jolted upon initial contact of the armature with each stop in each direction.

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