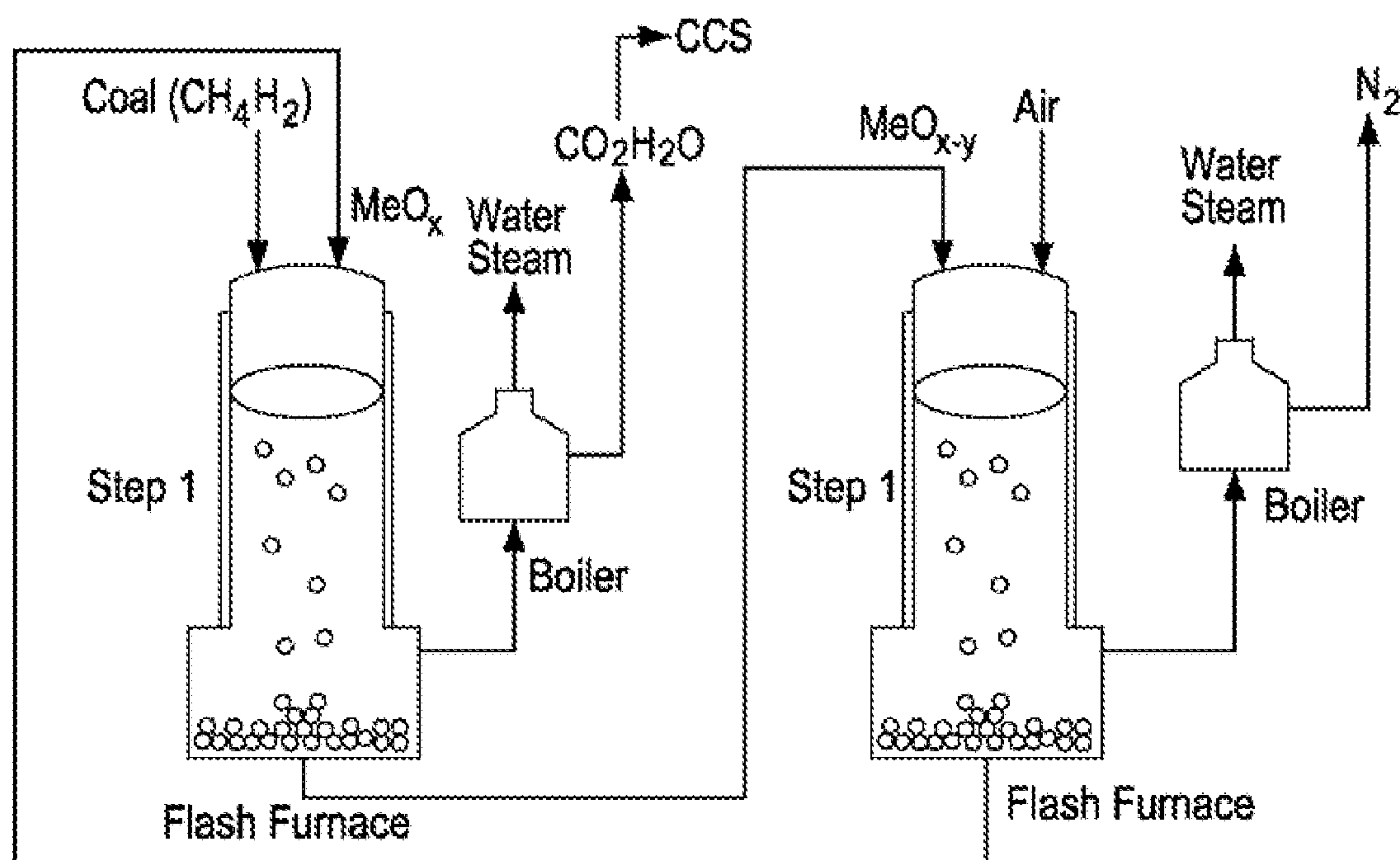


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(19) **United States**(12) **Patent Application Publication**
McHugh et al.(10) **Pub. No.: US 2011/0094226 A1**(43) **Pub. Date: Apr. 28, 2011**(54) **PROCESS AND APPARATUS FOR HIGH
ENERGY EFFICIENCY CHEMICAL
LOOPING COMBUSTION***F23C 9/06* (2006.01)*F23J 7/00* (2006.01)(52) **U.S. Cl. 60/645; 431/2; 431/4; 431/5; 110/204**(76) Inventors: **Lawrence F. McHugh**, North
Andover, MA (US); **Leonid N.
Shekhter**, Ashland, MA (US)(21) Appl. No.: **12/631,302**(22) Filed: **Dec. 4, 2009****Related U.S. Application Data**(60) Provisional application No. 61/255,716, filed on Oct.
28, 2009.**Publication Classification**(51) **Int. Cl.**
F01K 13/00 (2006.01)
F23L 7/00 (2006.01)
F23C 6/04 (2006.01)(57) **ABSTRACT**

Process and apparatus are provided for a high energy efficiency chemical combustion process. The process provides two reaction steps, both of which are exothermic. First, a reduced oxygen carrier is contacted with oxygen in a reactor to form an oxidized oxygen carrier, such as metal oxide or metal suboxide, and then the oxidized oxygen carrier is fed to a second reactor and combusted with a fuel. The reaction produces the reduced oxygen carrier and carbon dioxide. The reduced oxygen carrier from the second reactor is recycled back to said first reactor. Carbon monoxide can also be produced during the process depending on stoichiometric amounts of the reactants. Though the process can be performed in various types of reactor systems, one preferred embodiment is the flash furnace with the production of fly ash during combustion. The process is highly efficient and produces a large amount of usable work.

High Thermal Efficiency CLC Process Flowsheet

Enthalpy Change for Reduction Reactions with Carbon

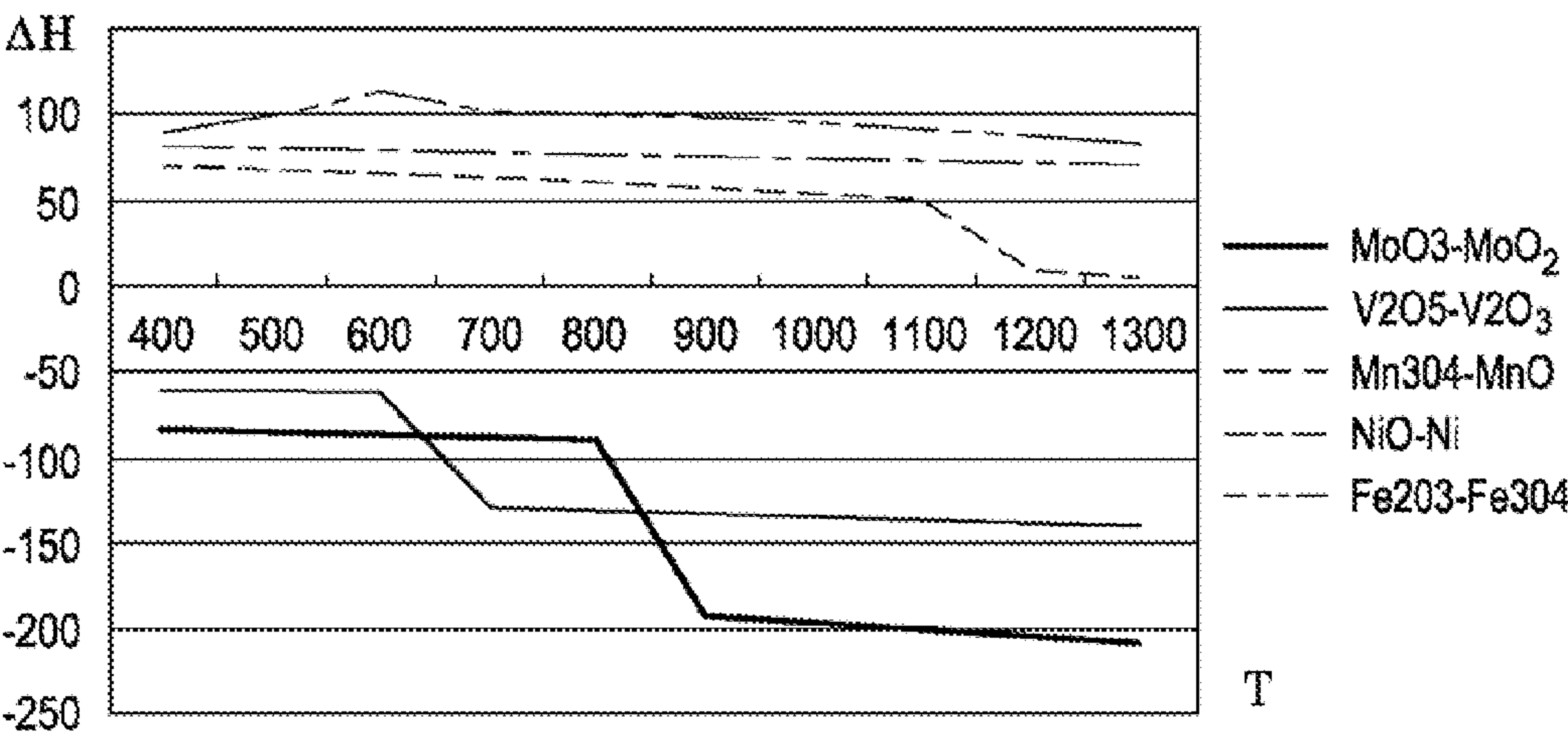


FIG. 1

Enthalpy Change for Reduction Reactions with Methane

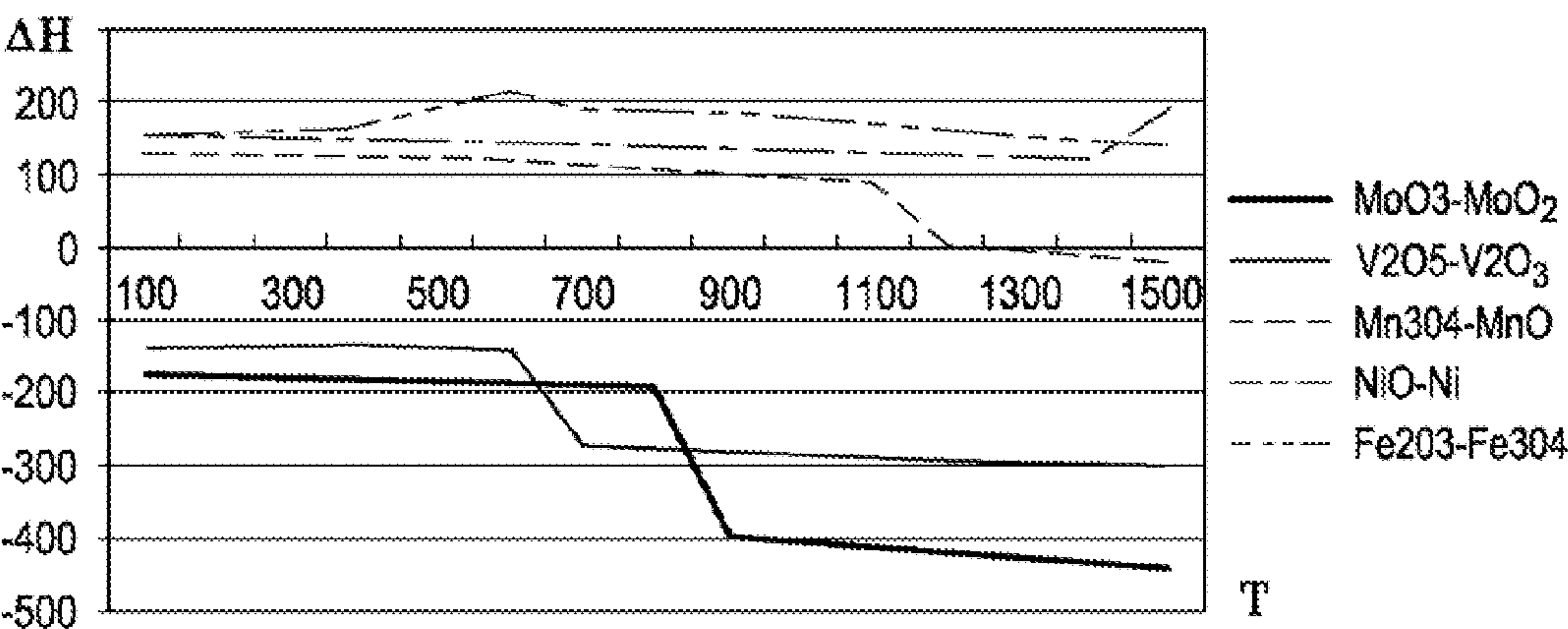


FIG. 2

High Thermal Efficiency CLC Process Flowsheet

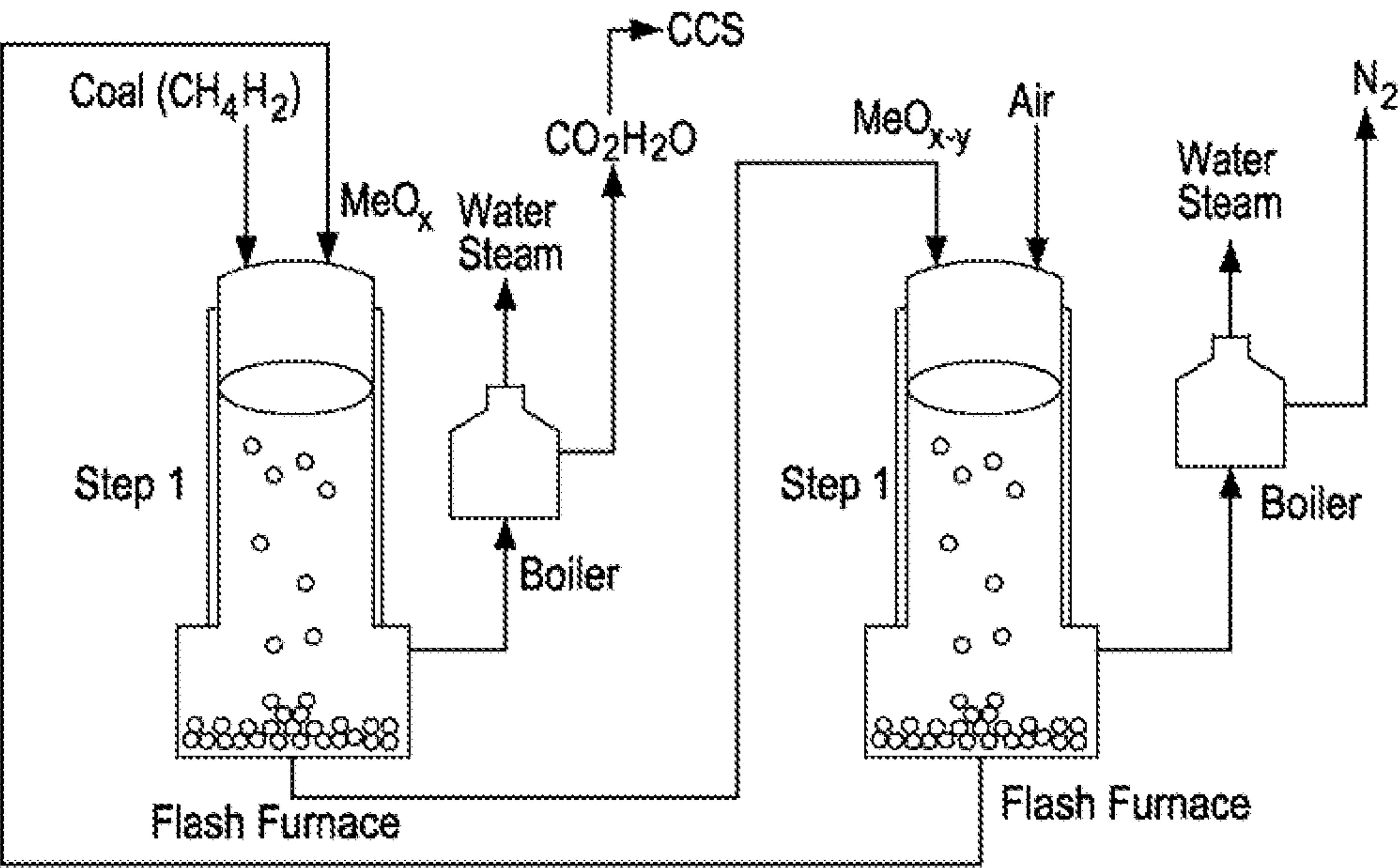


FIG. 3

Enthalpy Change for Reduction Reactions with Hydrogen

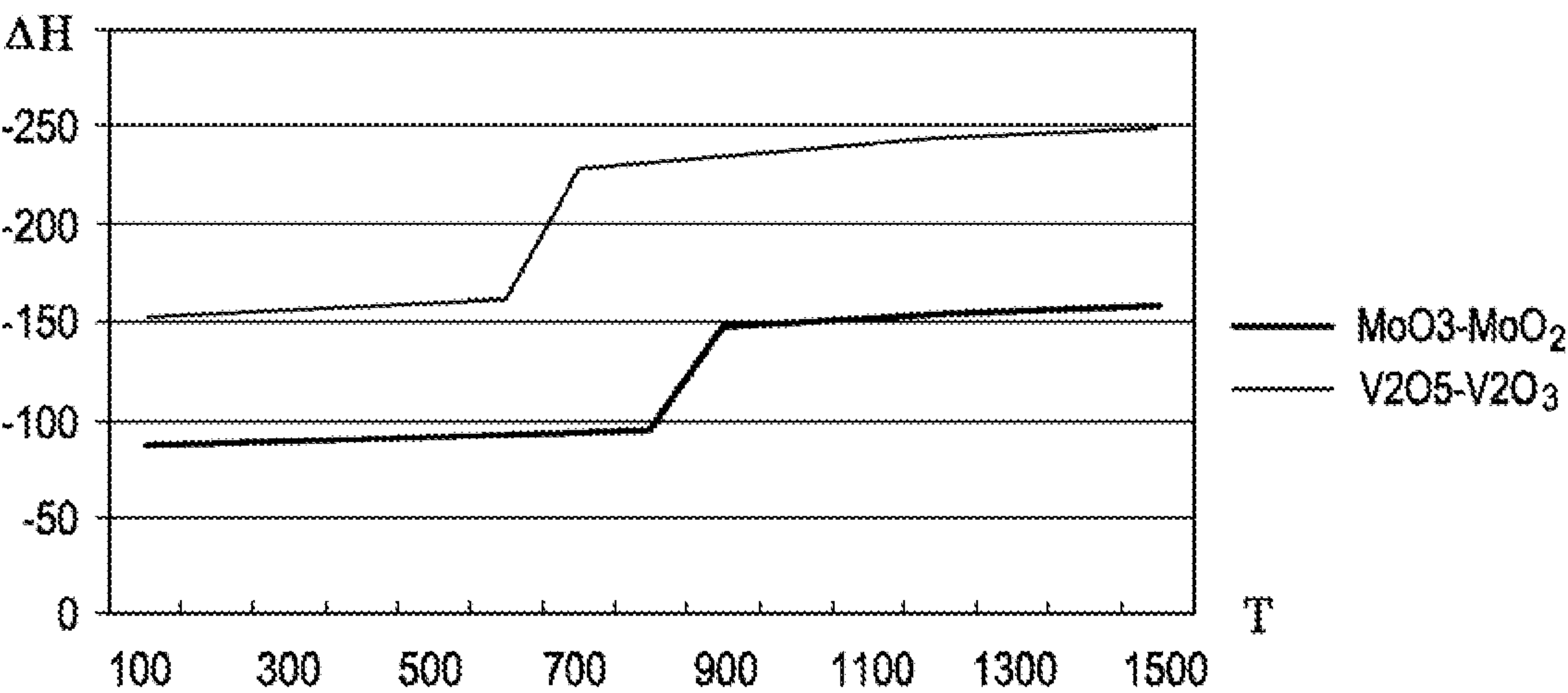


FIG. 4

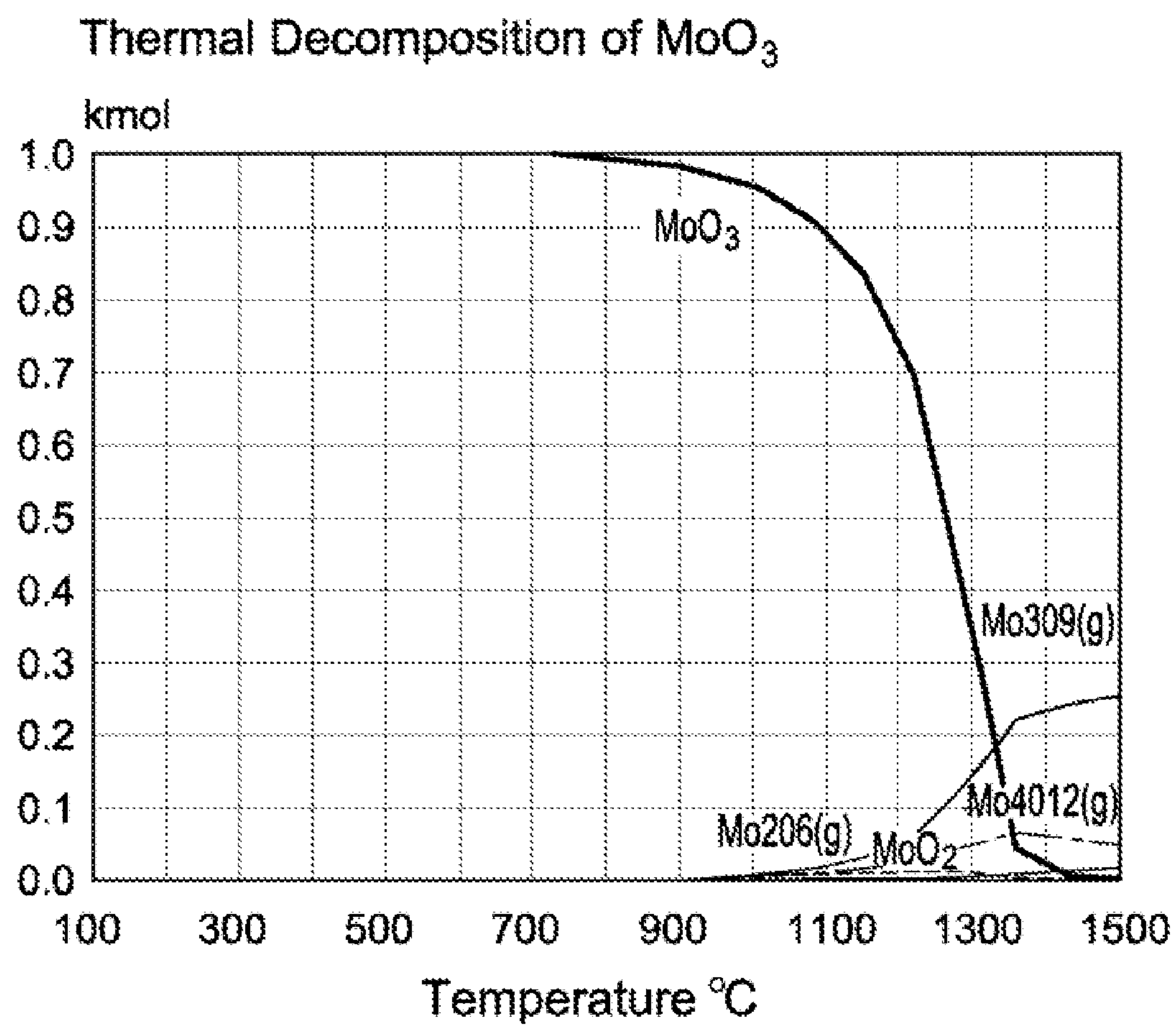


FIG. 5

Equilibrium Composition for the reduction of MoO₃ with Stoichiometric

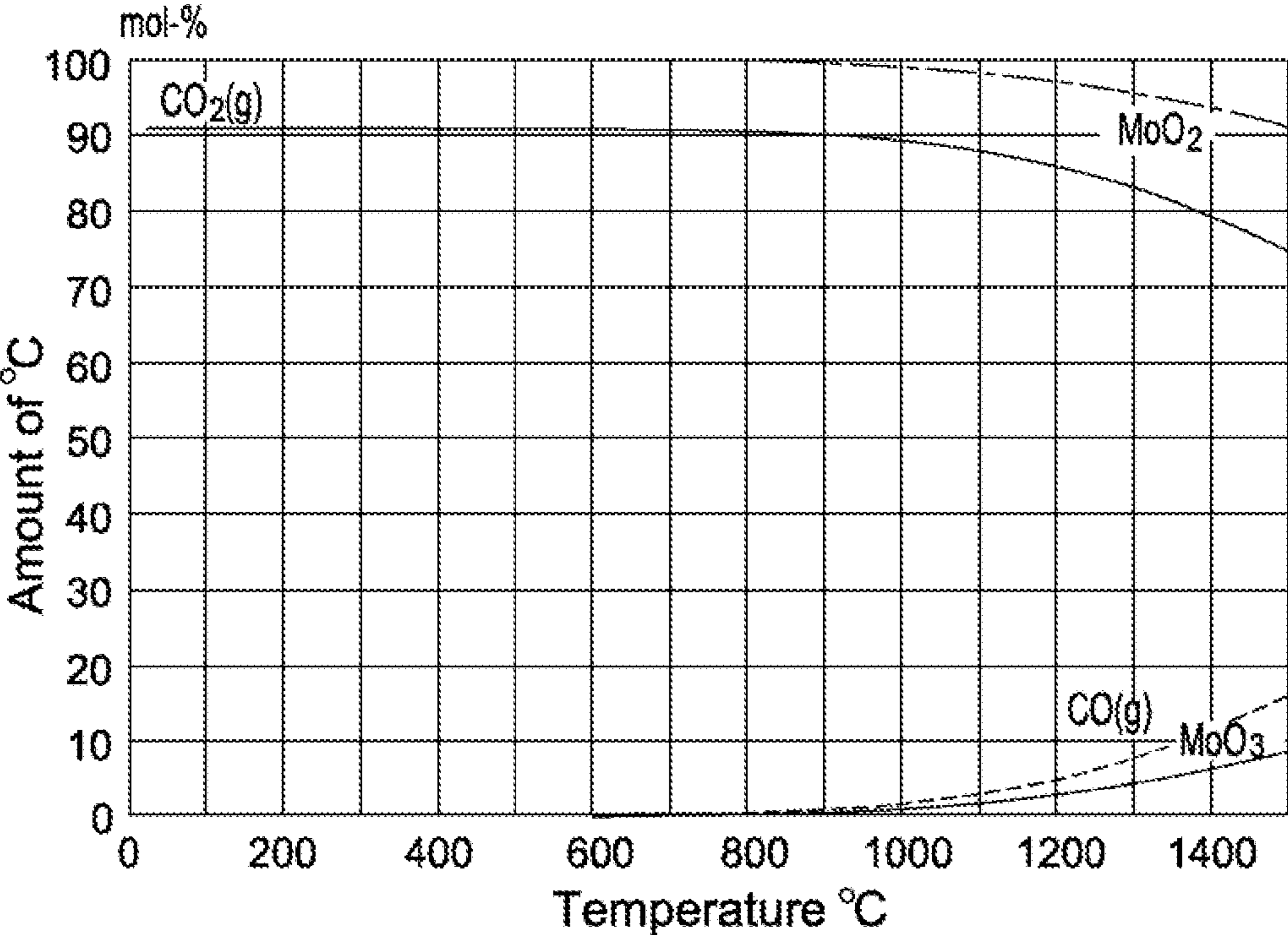


FIG. 6

Thermal Decomposition of Na₂O₂

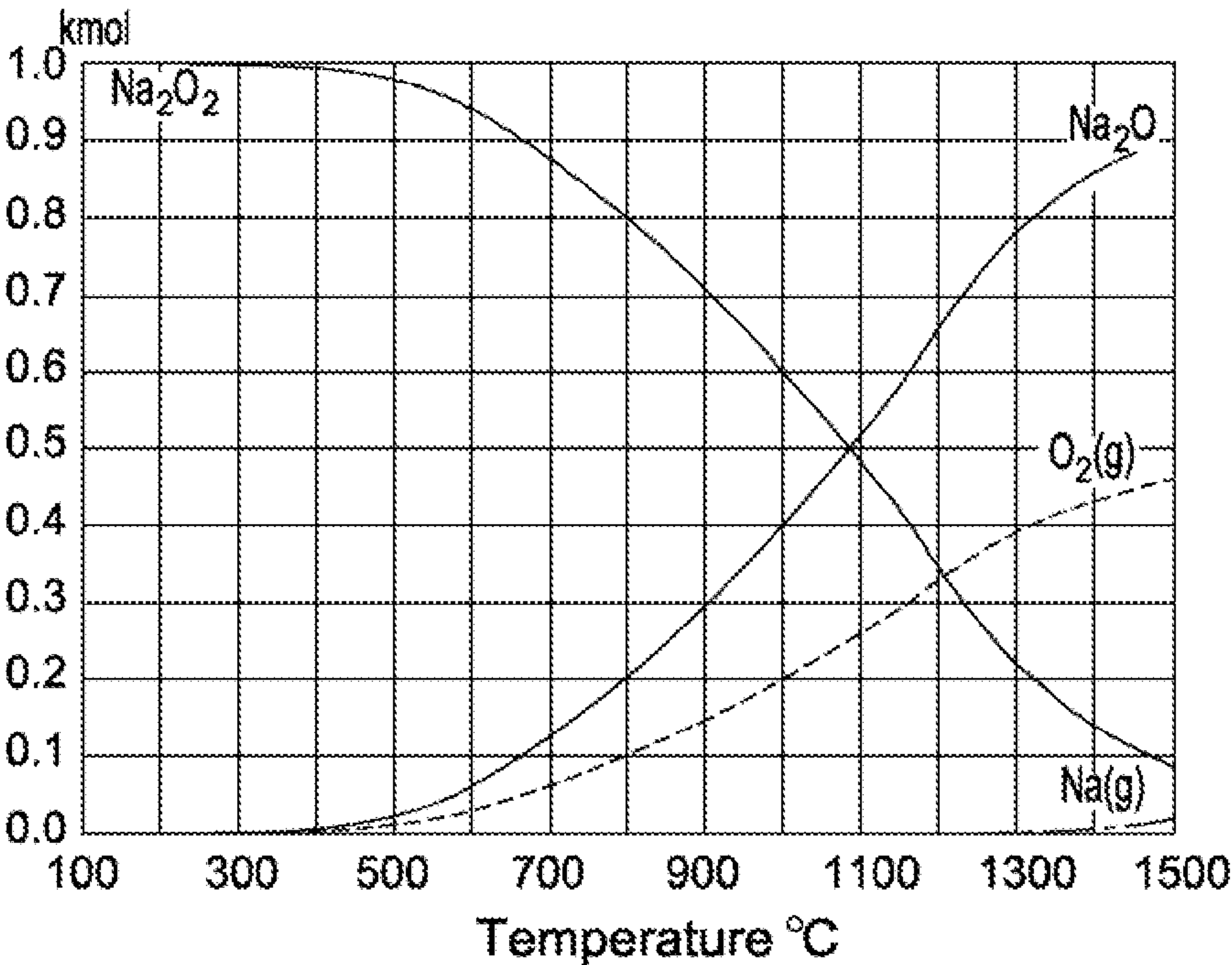


FIG. 7

Thermal Decomposition of MnO₂

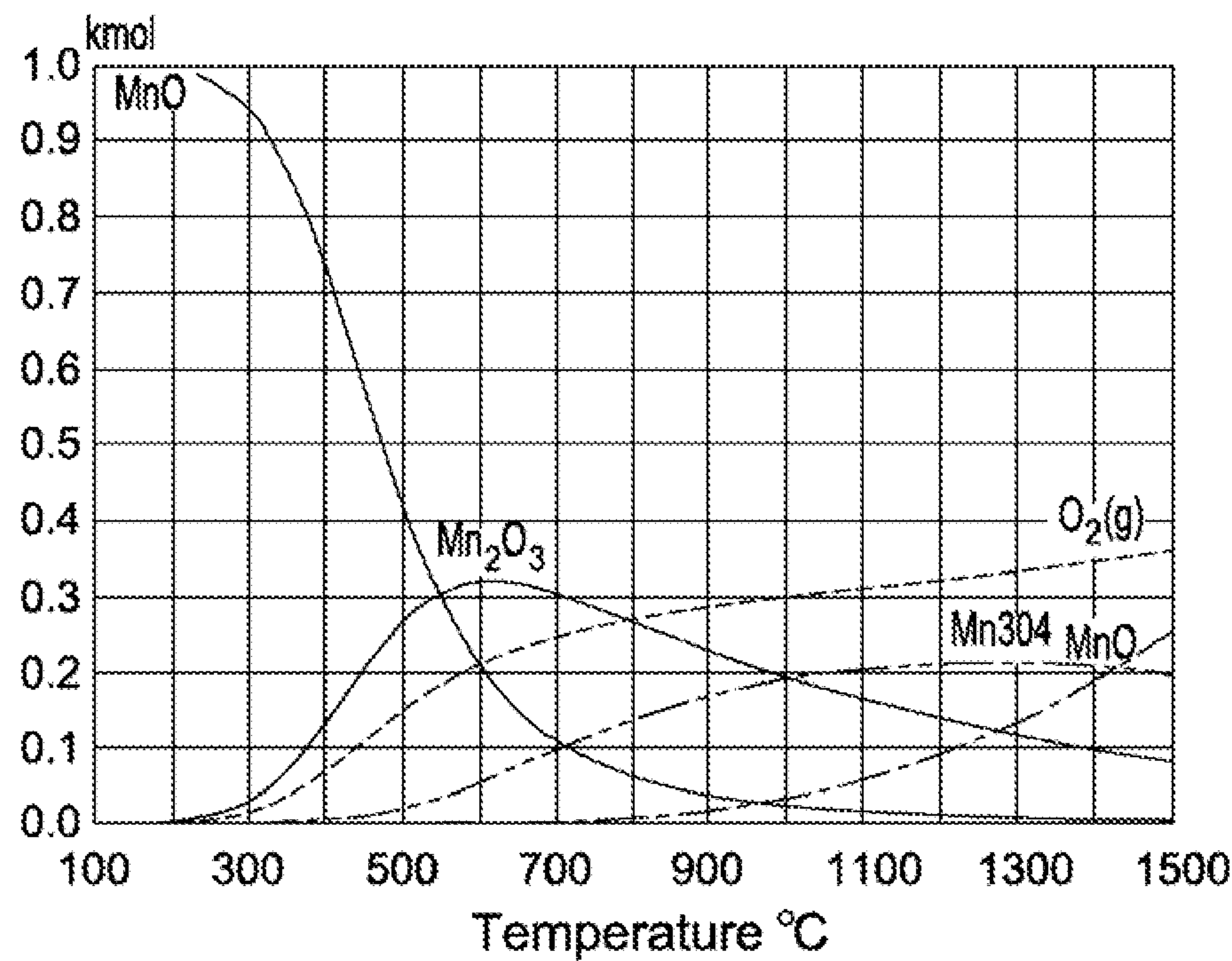


FIG. 8

Thermal Decomposition of Rh₂O₃

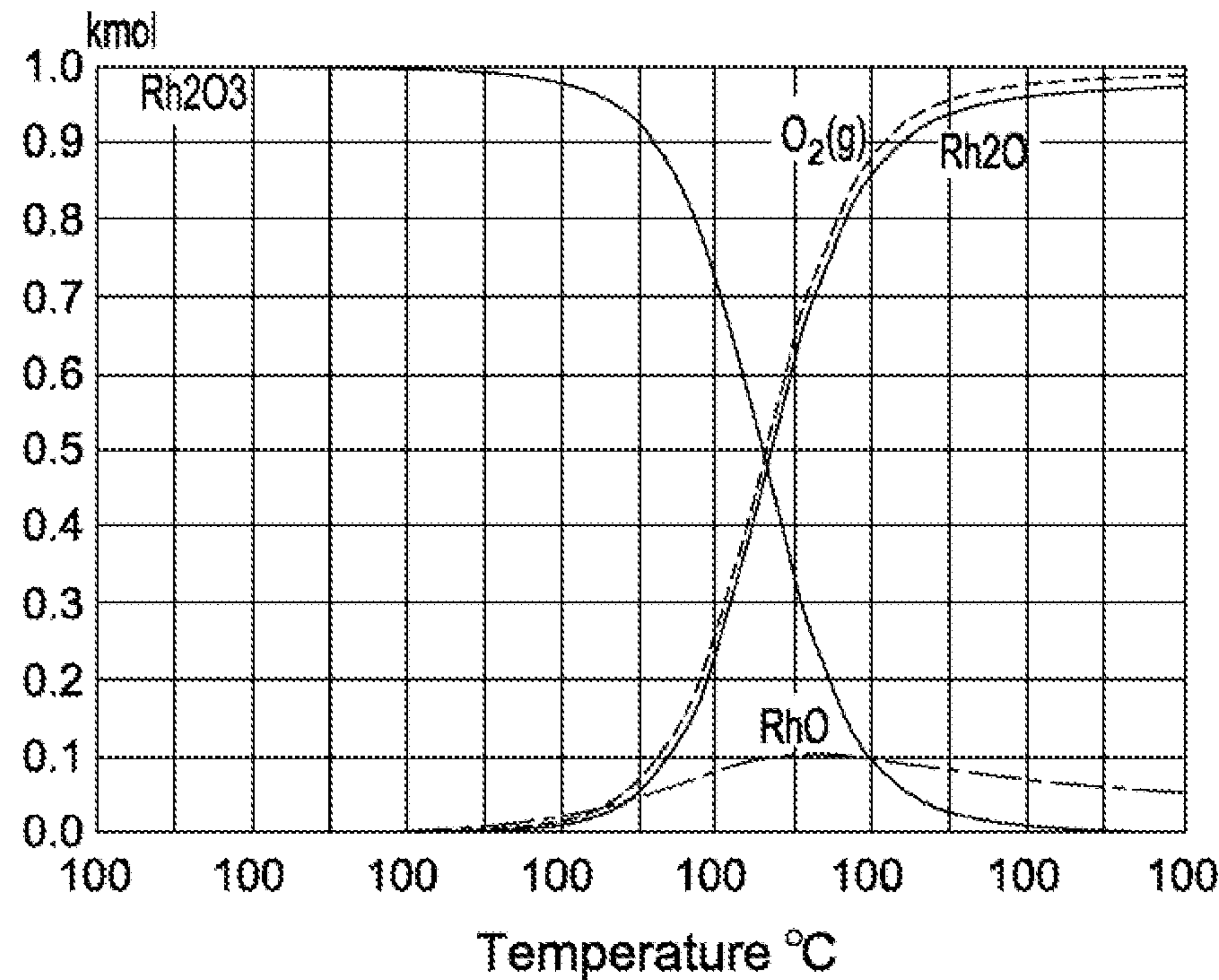


FIG. 9

Thermal Decomposition of PdO

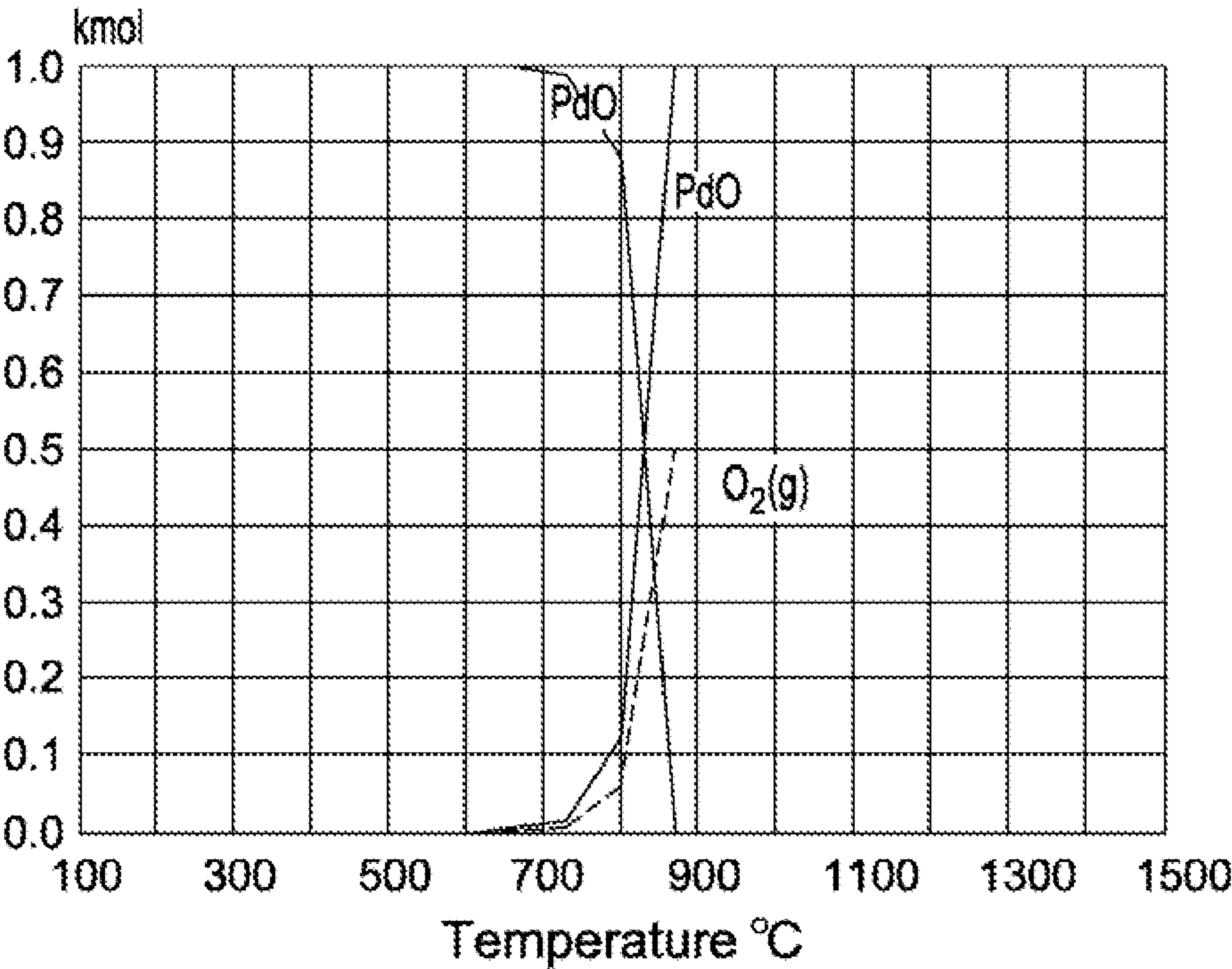


FIG. 10

Thermal Decomposition of PtO

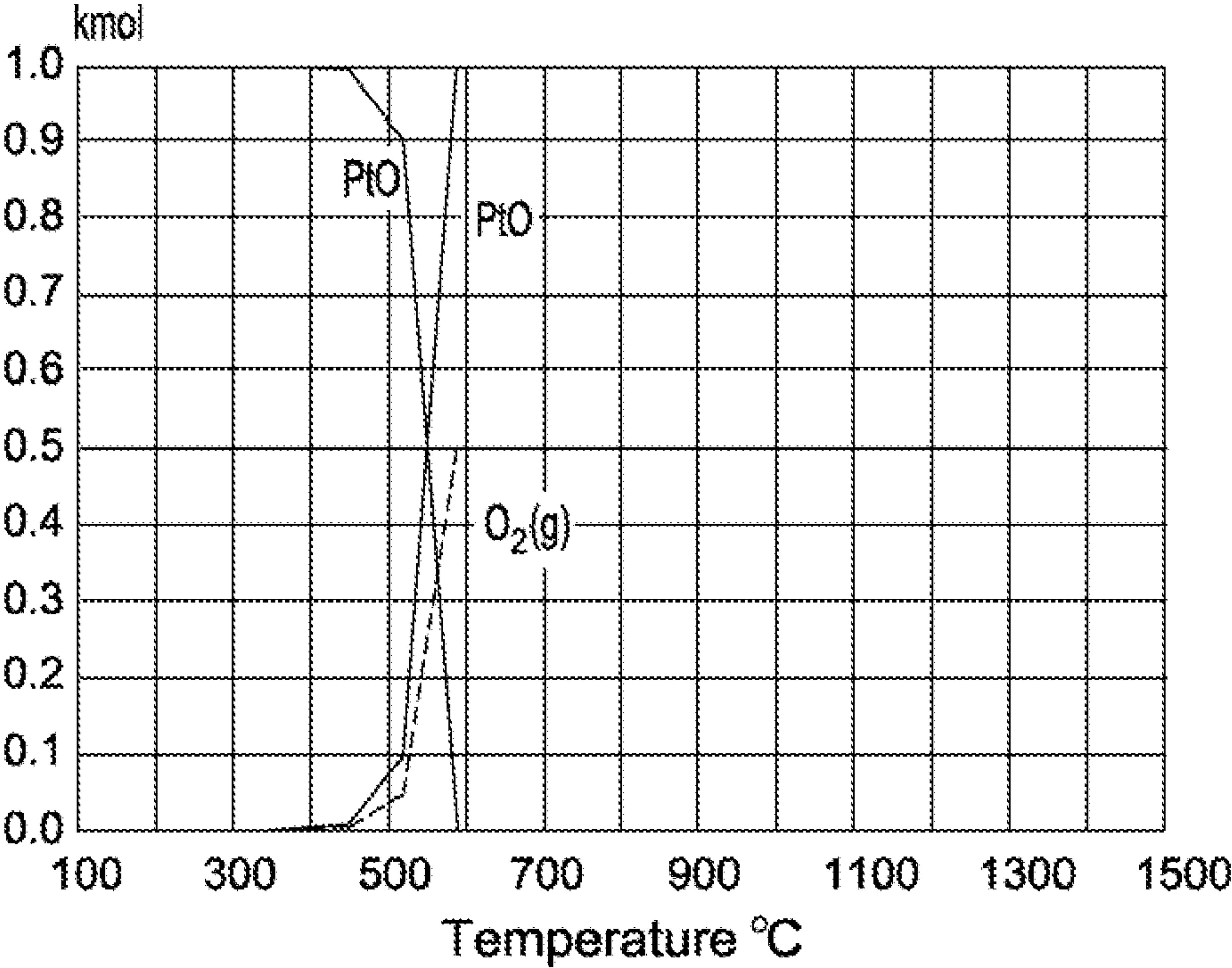


FIG. 11

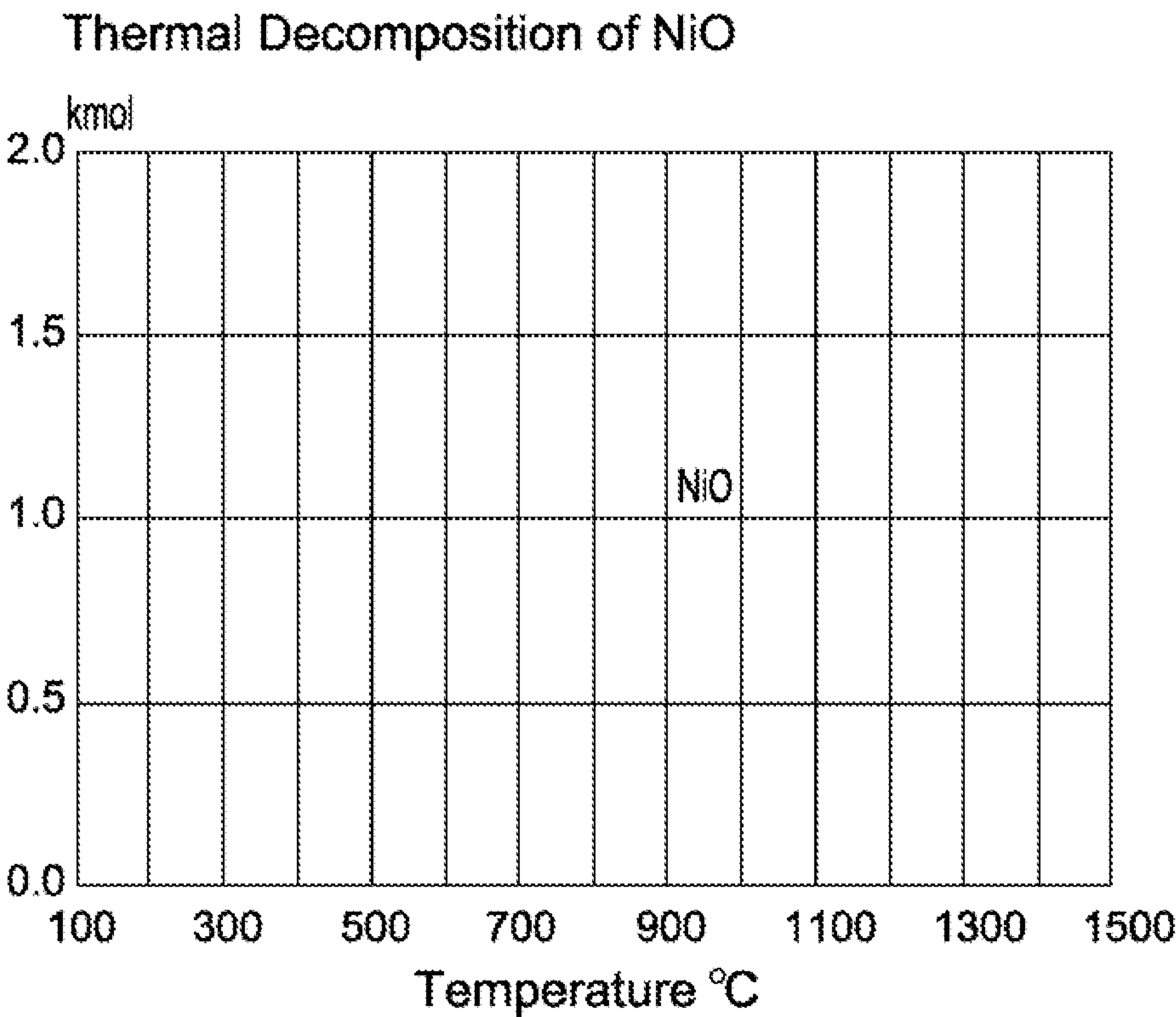


FIG. 12

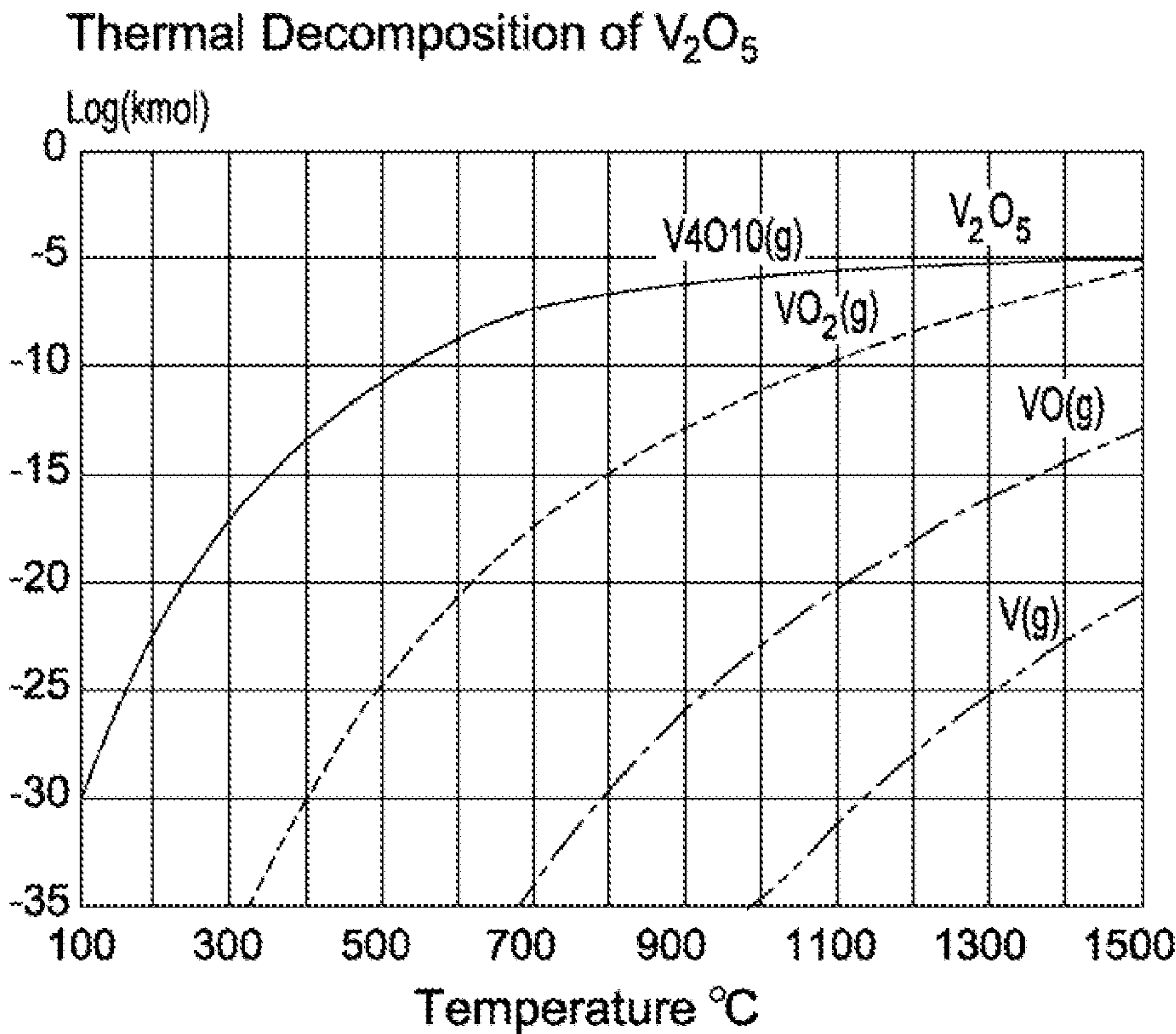


FIG. 13

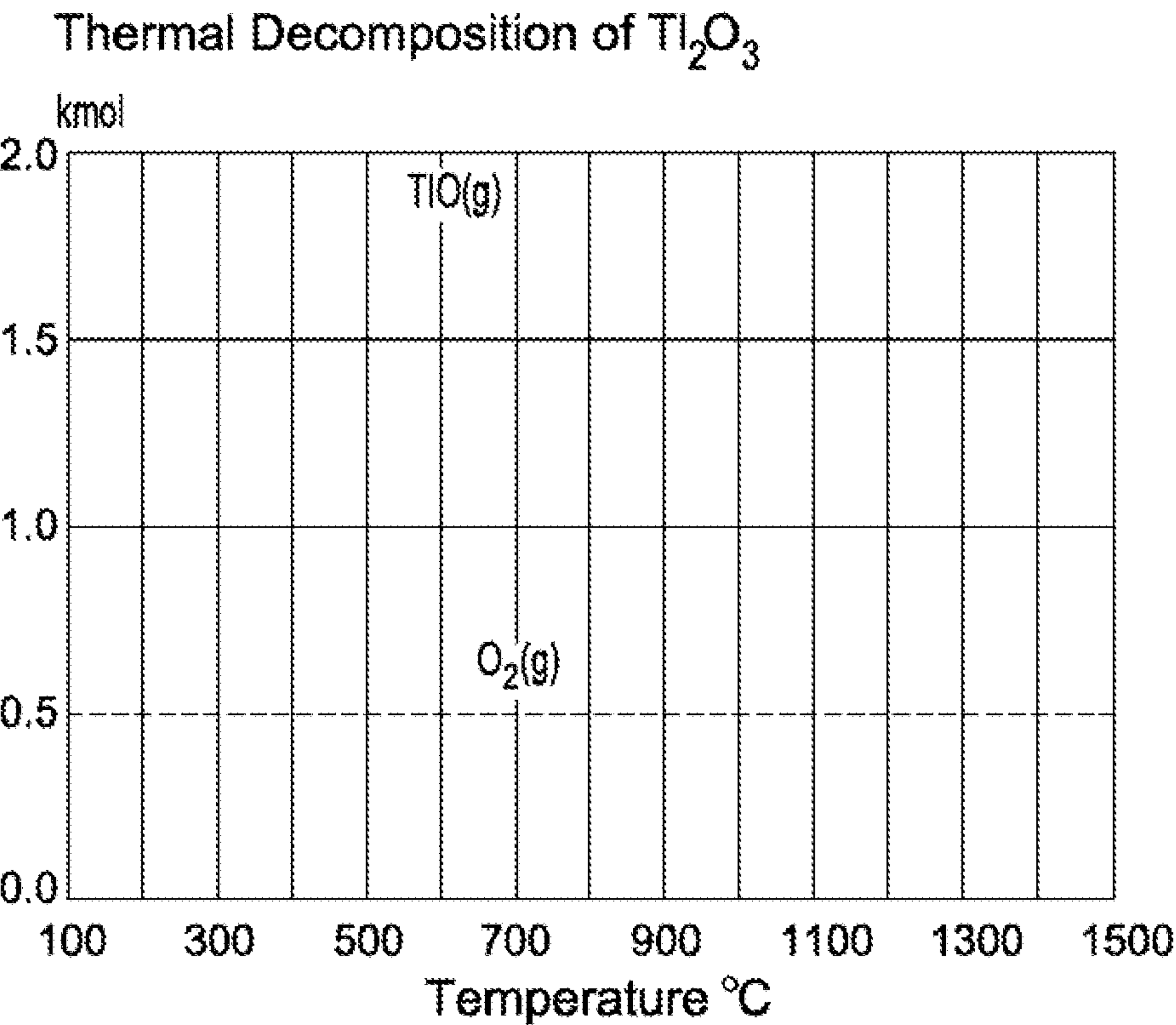


FIG. 14

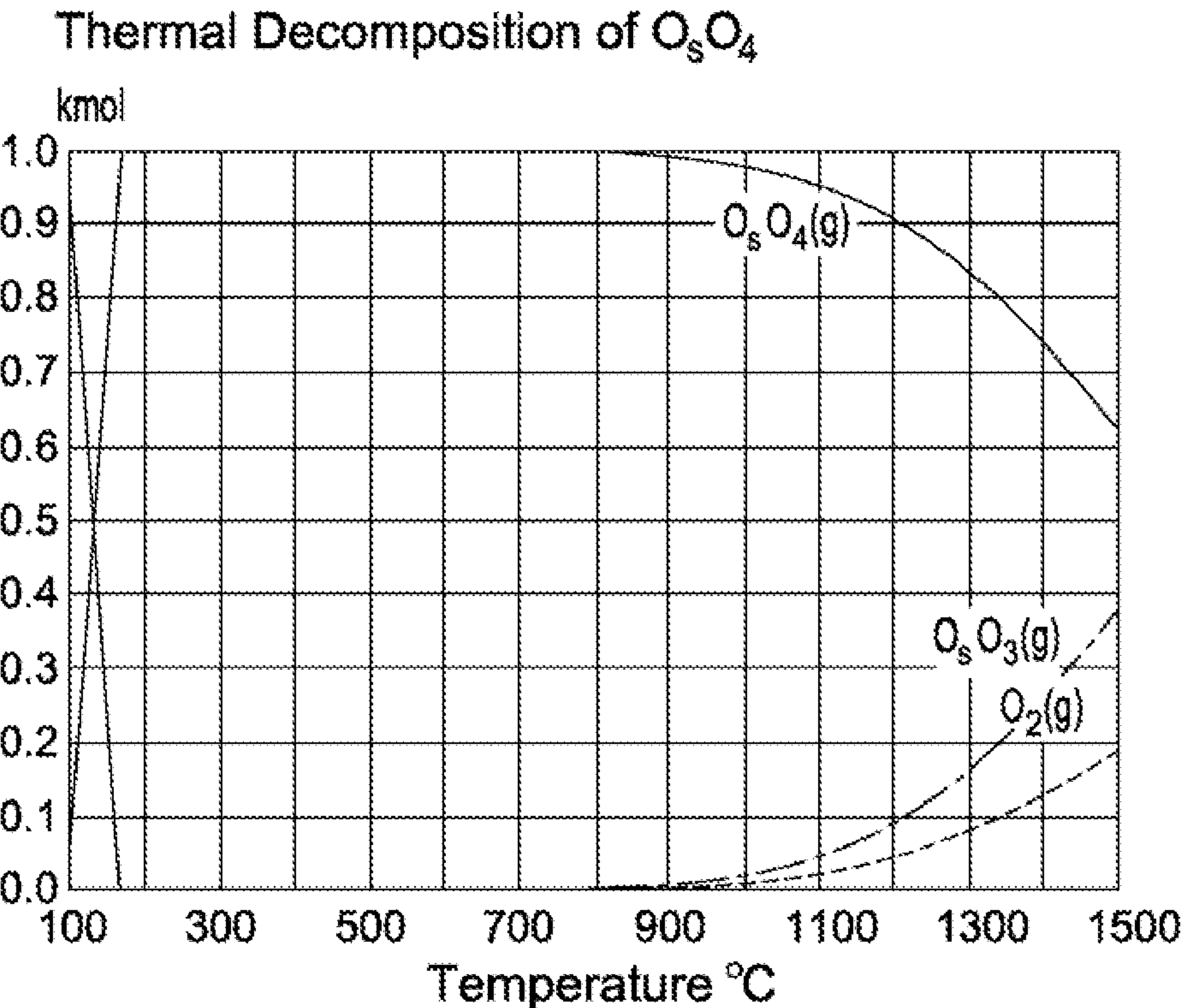


FIG. 15

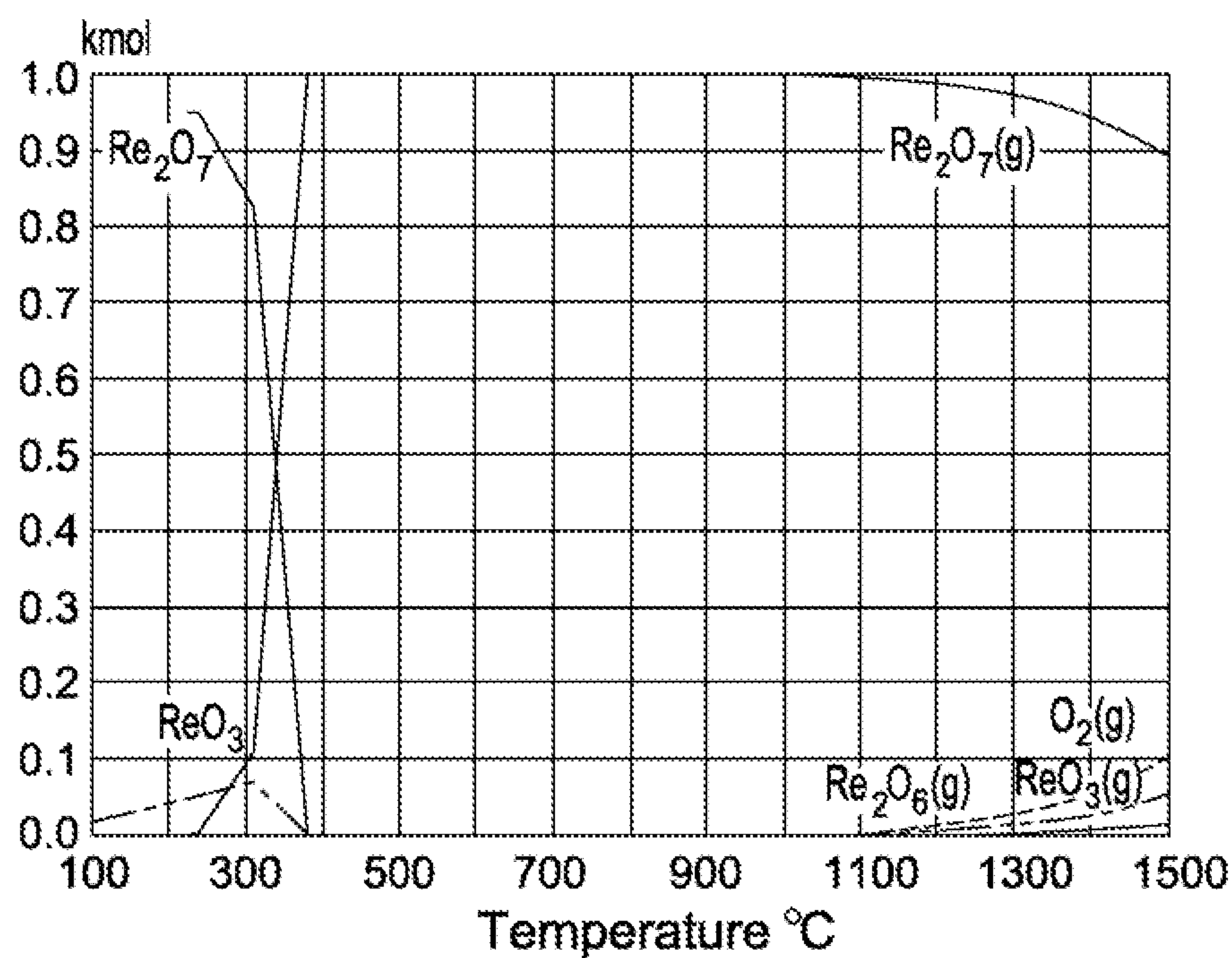
Thermal Decomposition of Re_2O_7 

FIG. 16

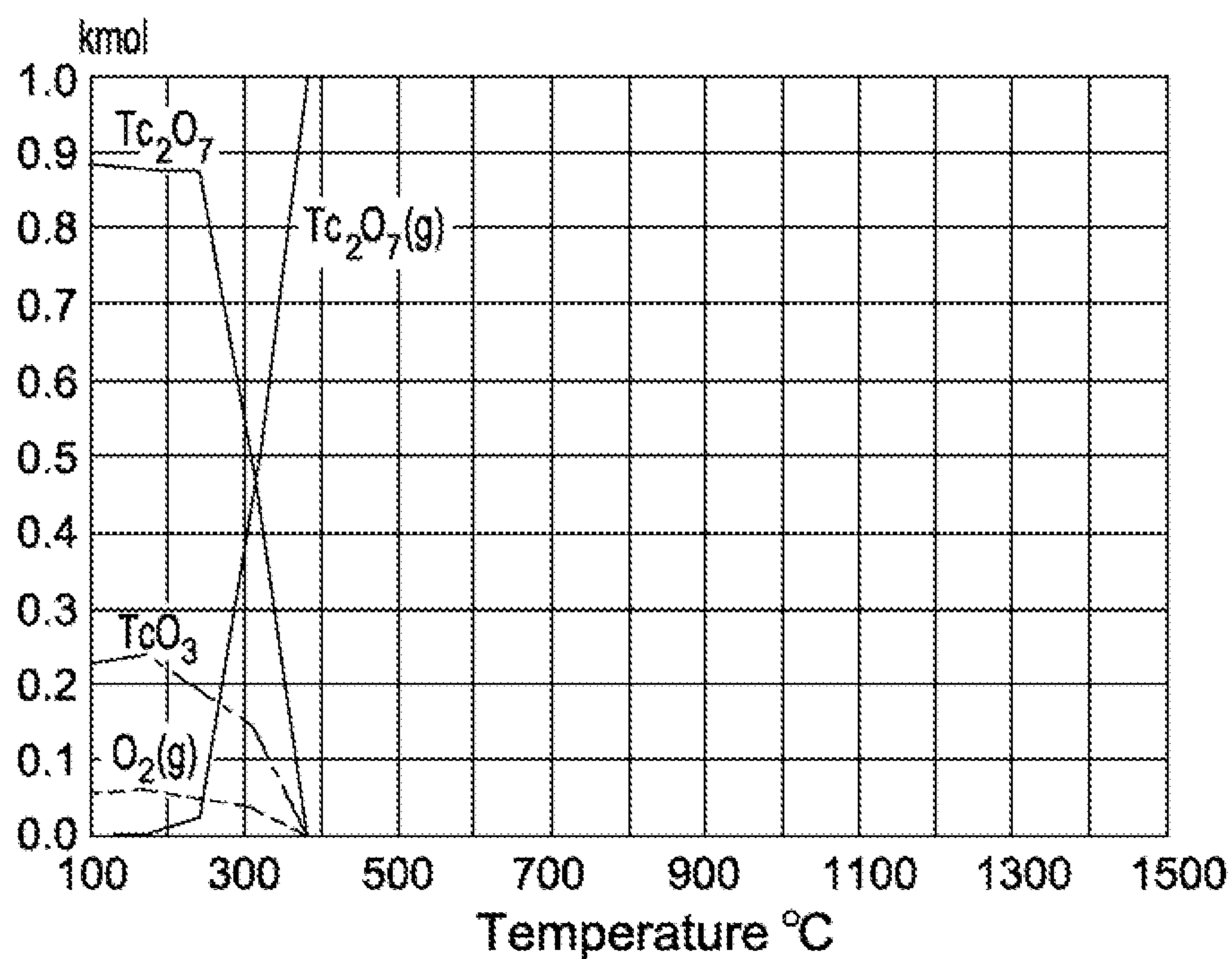
Thermal Decomposition of Tc_2O_7 

FIG. 17

Thermal Decomposition of CuO

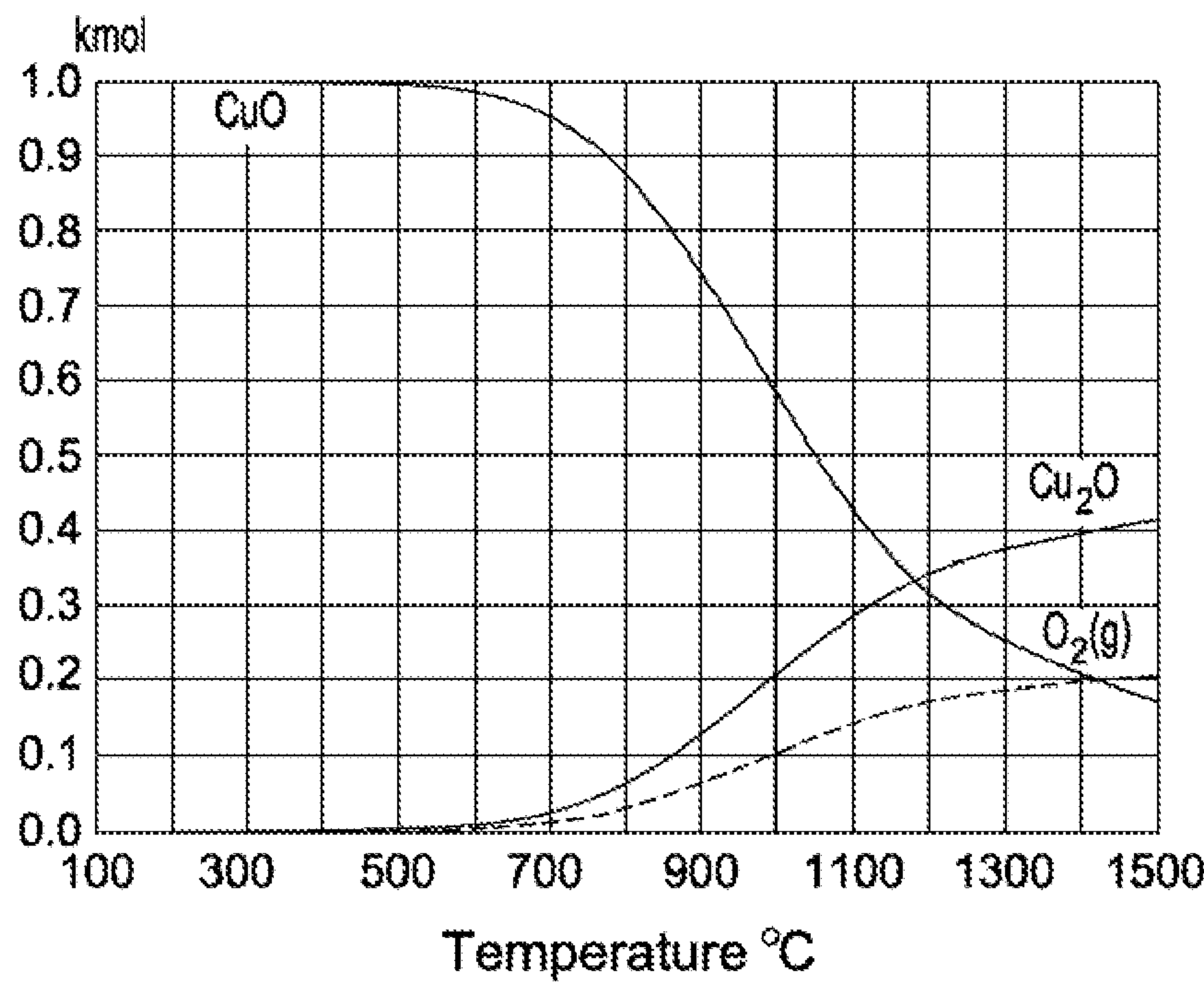


FIG. 18

Thermal Decomposition of BaO₂

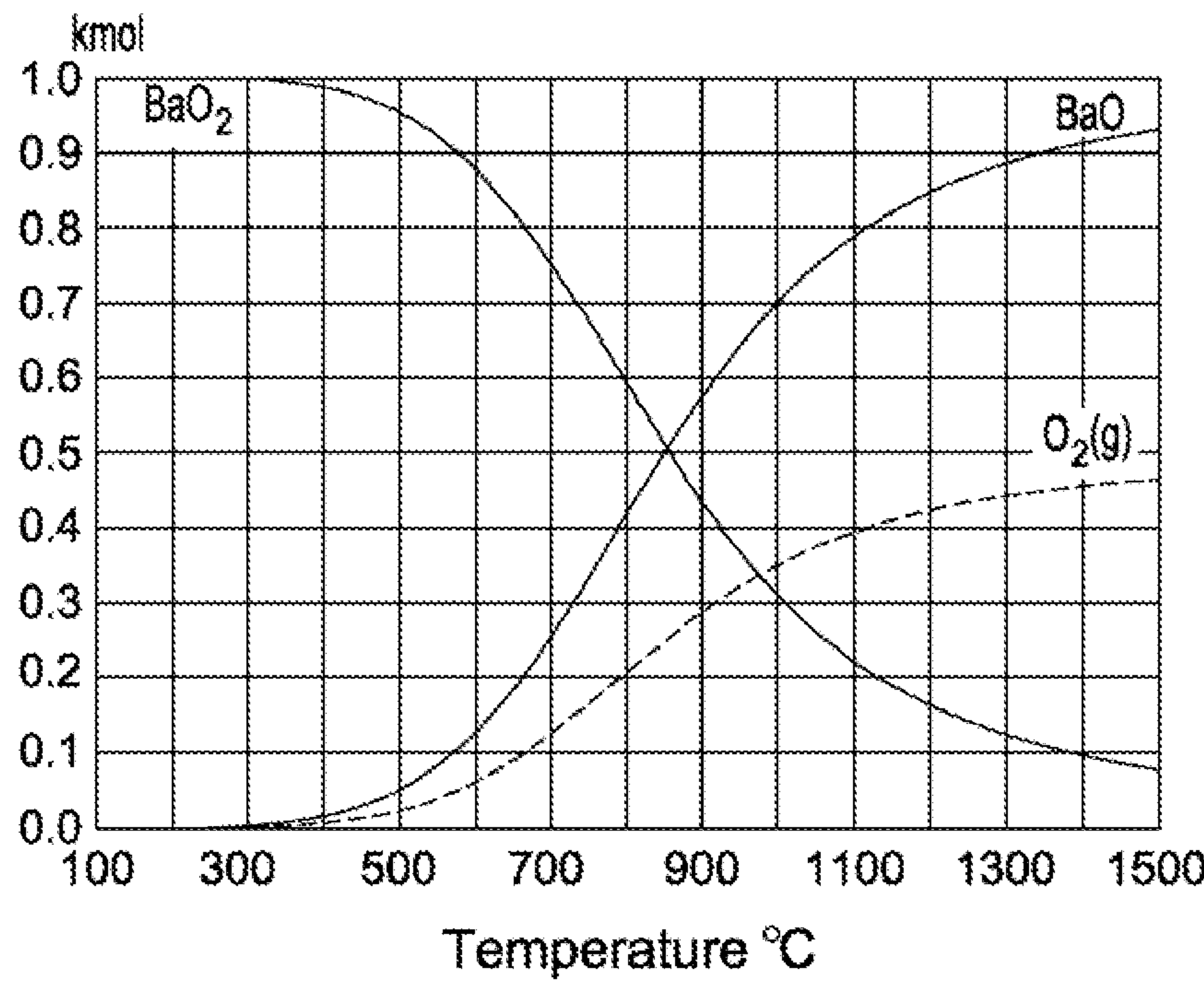


FIG. 19

Equilibrium composition for the reduction of carbon dioxide with carbon

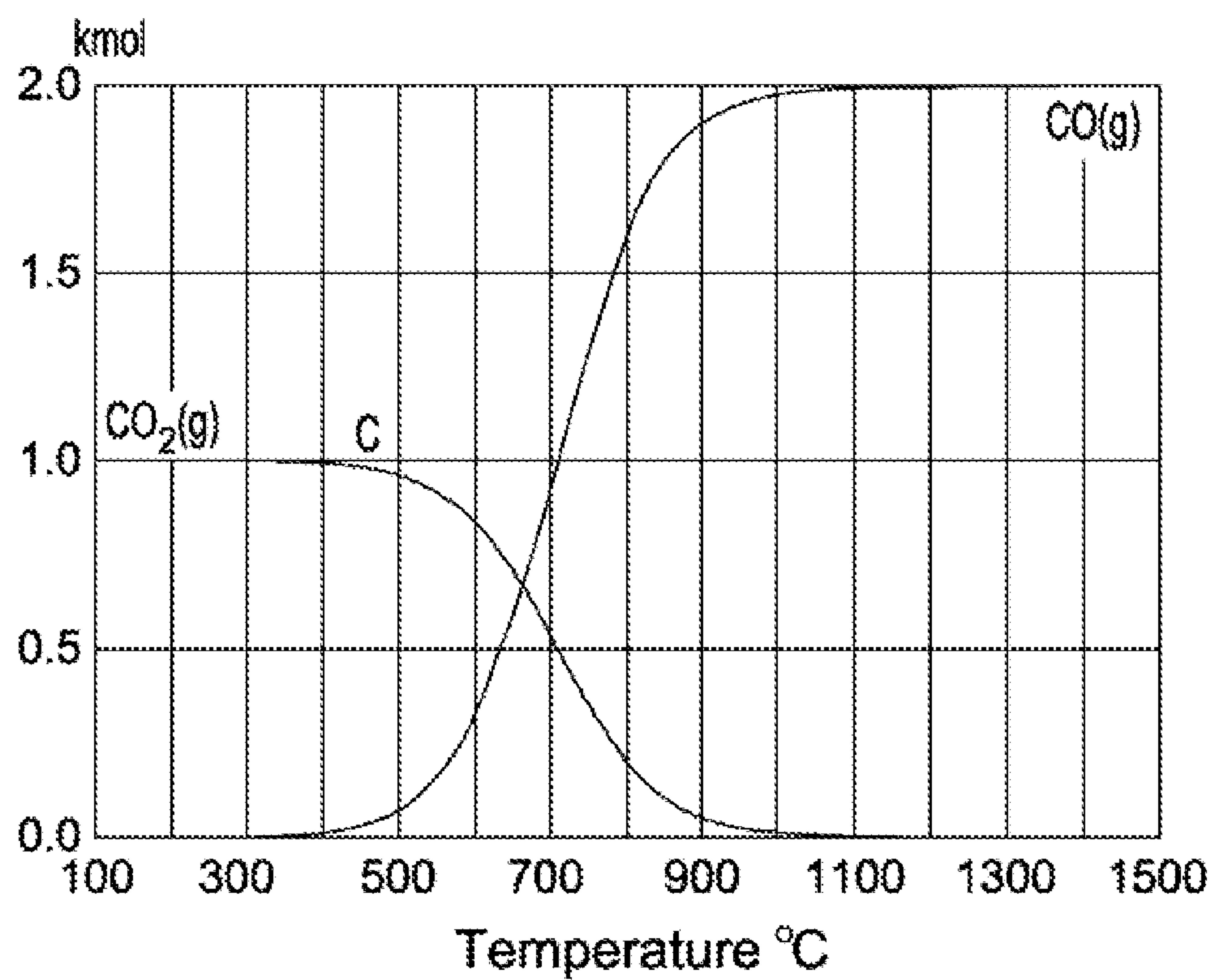


FIG. 20

PROCESS AND APPARATUS FOR HIGH ENERGY EFFICIENCY CHEMICAL LOOPING COMBUSTION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of prior-filed U.S. Provisional Patent Application Ser. No. 61/255,716, filed on Oct. 28, 2009, the subject matter of which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The present invention was not developed with the use of any Federal Funds, but was developed independently by the inventors.

FIELD OF THE INVENTION

[0003] The present invention relates to apparatus and methods of high efficiency generation of useful work via combustion, more specifically, in combustion looping systems, for high efficiency energy production and more particularly, the chemical looping combustion in furnaces of fuel sources using metal oxides. The invention relates to clean coal technology with carbon dioxide capture and sequestration. The invention also relates to the removal of fly ash produced during the combustion process that can be further utilized in ferroalloy processes.

BACKGROUND OF THE INVENTION

[0004] The burning of fuels is currently the main mechanism that the world utilizes in order to meet its energy needs. Global warming is the increase in the average temperature of the Earth's near-surface air and oceans. Global warming was first noticed in the mid-20th century and scientists have projected its continuation. The Intergovernmental Panel on Climate Change (IPCC) has noted that the global surface temperature has increased $0.74 \pm 0.18^\circ \text{C}$. ($1.33 \pm 0.32^\circ \text{F}$.) during the last century. The IPCC also concludes that although variations in natural phenomena such as solar radiation and volcanoes produced most of the warming from pre-industrial times to 1950 and had a small cooling effect afterward, most of the observed temperature increase since the middle of the 20th century was caused by increasing concentrations of greenhouse gases resulting from human activity such as fossil fuel burning and deforestation. Although not unanimous, these basic conclusions have been endorsed by more than 40 scientific societies and academies of science, including all of the national academies of science of the major industrialized countries. The basic argument that greenhouse gases keep the Earth comfortably warm has never been challenged and it follows that an increase in carbon dioxide in the atmosphere undoubtedly produces a rise in temperature at ground level.

[0005] It is known that naturally occurring greenhouse gases have a warming effect by trapping heat radiated from the sun. The major greenhouse gases are water vapor, carbon dioxide (CO_2), methane (CH_4), sulfur dioxide (SO_2) and ozone (O_3). Clouds also affect the radiation balance, but they are composed of liquid water or ice and so are considered separately from water vapor and other gases. CO_2 concentrations in the atmosphere are continuing to rise due to the continual burning of fossil fuels and land-use change.

[0006] Currently, the amount of carbon dioxide in the atmosphere is increasing at the rate of about one part per million per year. If this continues, some meteorologists expect that the average temperature of the earth will increase by about 2.5 degrees Celsius. Such changes could be enough to cause glaciers to melt, which would cause coastal flooding. Today the amount of carbon dumped globally into the atmosphere corresponds, on average, to one ton per person on the planet, each year. Because carbon-based energy is especially important in the United States, the average American per capita emission is 5 tons of carbon annually.

[0007] Among the fossil fuels, coal is the most carbon intensive so energy generated by coal produces the highest carbon dioxide emissions. Coal is the second largest domestic contributor to carbon dioxide emissions in the United States. Currently about fifty percent of the energy in the United States is generated from coal, with more than 500 coal-fired power plants in the United States. U.S. coal burning power plants contribute 1.5 billion tons per year of carbon dioxide. Coal is found in abundance in various countries, including the United States, India and China. The supply of coal in the United States is projected to last for up to 250 years. It is currently thought that coal will continue to be used to meet the world's energy needs in significant quantities throughout the world because coal is plentiful and relatively less expensive than other energy producing technologies. Globally, coal is responsible for 40% of carbon dioxide emissions. The International Energy Agency predicts that China will surpass the United States in carbon dioxide emissions by the end of 2009 and China continues to build new coal-fired power plants for its energy needs.

[0008] In 2006, environmental groups pushed for legislation that would reinstate CO_2 as a pollutant. In August of 2006, EPA General Counsel Robert Fabricant concluded that since the Clean Air Act does not specifically authorize regulation to address climate change, CO_2 is not a pollutant. Nonetheless, the public has become more concerned about global warming which has led to new legislation. US power plants face pressure to reduce CO_2 emissions. The coal industry has responded by running advertising campaigns touting clean coal in an effort to counter negative perceptions, as well as by putting more than \$50 billion towards the development and deployment of clean coal technologies, including carbon capture and storage. The expenditure has been unsuccessful to date in that there is not a single commercial scale coal fired power station in the United States that captures and stores more than token amounts of carbon dioxide.

[0009] European power plants are also faced with reducing their CO_2 emissions significantly by 2012 as required by the Kyoto Protocol. Energy producers have embarked upon a unique way to reduce the CO_2 emitted into the atmosphere via a technique known as carbon capture and storage which involves siphoning off and burying the CO_2 underground. While the CO_2 is not eliminated, it is contained. The Department for Environment Food and Rural Affairs is working out plans to give industries credit for carbon capturing and storing in the second phase, from 2008-12, of the European carbon trading scheme. Such technologies, however, also have potential negative effects on the environment, such as underground leaking, contamination of waters, and potential health effects on plants and animals. Geological structures used to store carbon dioxide need to be able to remain stable and retain their capacity for hundreds or even thousands of years.

Thus, these technologies are in development and testing and are not yet considered to be a final solution for carbon dioxide reduction in the atmosphere.

[0010] Carbon capture and sequestration can reduce carbon dioxide emissions significantly, while allowing the use of coal as a fuel source. First, coal is collected in a gasifier with oxygen and steam where heat and pressure are used to form a synthetic gas, known as “syngas”. The carbon dioxide can then be captured. The syngas is composed of carbon monoxide and hydrogen. Potential uses of syngas include power generation and fertilizers.

[0011] After being captured as a gas from the separation stage, the carbon dioxide can be compressed to supercritical fluid and/or cooled to decrease its volume. Tankers, trucks and ships are used for bulk transport over short distances and in small to moderate scales. For larger plants, a pipeline is usually the practical alternative for transportation of carbon dioxide.

[0012] The CO₂ can be sent to food production, such as incorporation into soft drinks or to the agricultural industry as a viable ingredient in feedstock, or it can be contained for geological storage.

[0013] Typical carbon dioxide sequestration technologies include coal beds, depleted oil and gas reservoirs, and saline aquifers. Carbon dioxide can also be dissolved in the ocean deeper than half a mile, or deposited on the sea floor more than two miles down in liquefied form. Unfortunately, some sequestration technologies are still subject to potential leaks into the environment with harmful consequences. Geological structures used to store carbon dioxide need to be able to remain stable and retain their capacity for hundreds or even thousands of years. Thus, the optimal solution to the carbon dioxide problem is to minimize its emission.

[0014] In addition to CO₂, various other emissions are produced during fuel combustion processes, including sulfur dioxide, nitrogen oxides and mercury. It has been found that these pollutants also promote the greenhouse effect as well as the reduction of the ozone layer in the stratosphere. Extensive research of these emissions has been carried out in recent years.

[0015] Of course, the best alternative to avoid greenhouse effects and other negative environmental consequences would be to find a way to eliminate or minimize the production of CO₂ and other pollutants during the process of power generation. Thus, a focus has developed on methods of high efficiency energy production.

[0016] Clean coal technology is an umbrella term used to describe technologies being developed that aim to reduce the environmental impact of coal energy generation. These technologies include chemically washing minerals and impurities from the coal, gasification, treating the flue gases with steam to remove sulfur dioxide, carbon capture and storage technologies to capture the carbon dioxide from the flue gas and dewatering lower rank coals (brown coals) to improve the calorific quality, and thus the efficiency of the conversion into electricity.

[0017] Clean coal technology usually addresses atmospheric problems resulting from burning coal. Historically, the primary focus was on sulfur dioxide and particulates, since it is the most important gas in the causation of acid rain. More recent focus has been on carbon dioxide. Concerns exist regarding the economic viability of these technologies and the timeframe of delivery, potentially high hidden economic

costs in terms of social and environmental damage, and the costs and viability of disposing of removed carbon and other toxic matter.

[0018] The world’s first “clean coal” power plant went on-line in September 2008 in Spremberg, Germany. The plant is state-owned and has been built by the Swedish firm Vattenfall. The plant is state owned because of the high costs of this technology. Private investors often invest in other sources of power such as nuclear, solar and wind power generation technologies. The facility captures carbon dioxide and acid rain producing sulfides, separates them, and compresses the carbon dioxide into a liquid state. It has been planned to inject the carbon dioxide into depleted natural gas fields or other geological formations.

[0019] In conventional pulverized coal-fired power plants and Super Critical Pulverized coal technologies (SCPC) that produce flue gases, the carbon dioxide is separated out of the flue gases. Typical CO₂ capture is in the range of 80 to 95%. The flue gas is passed through an absorber where a solvent removes most of the carbon dioxide. In Integrated Gasification Combined-Cycle technology (IGCC), which is utilized in newer power plants and well suited for high grade bituminous coal, about 90% of the CO₂ is removed. Syngas is cooled and cleaned to remove particulates and other emissions. It is then combusted with air or oxygen to drive turbine engines. Exhaust gases undergo heat exchange with water and steam to drive steam turbines and power generators.

[0020] A major disadvantage to IGCC technology and SCPC technologies are the major technical modifications required for retrofitting existing power plants, involving massive costs. In fact, engineering estimates show it may prove that it would be less expensive to destroy existing power plants and build new ones rather than to retrofit the existing facilities. Such costs may thus prove prohibitive for implementing clean air technology.

[0021] Another technology option for reducing carbon dioxide emissions is Underground Coal Gasification (UCG). This technology however, presents other environmental concerns associated with coal mining. Oxygen fired pulverized coal combustion appears to be more promising for lower quality coals. The process involves burning coal in an oxygen-rich atmosphere to produce a pure stream of carbon dioxide.

[0022] Chemical Looping Combustion (CLC) has presented itself as a viable technology for improved fuel combustion and power generation. First introduced in 1954, in 1983 chemical looping combustion was presented as a way of increasing the thermal efficiency of power plants, and in the 1990’s, it was recognized as a possibility to capture carbon dioxide from fossil fuels in order to reduce climate impact. CLC is a combustion technology where no direct contact occurs between air and fuel. It is an emerging technology that enables carbon dioxide capture without the high efficiency loss of current carbon capture technologies.

[0023] The chemical looping combustion process for hydrocarbons or hydrogen based fuels that has been developed to date is a process in which metal-based oxygen carriers undergo repeated reduction/oxidation cycles to allow for combustion without the fuel coming into contact with air. In the simplest form of CLC, an oxygen carrying species, normally a metal or metal suboxide is first oxidized in air forming a metallic oxide. This oxide is then utilized as the oxygen source for the oxidation of the fuel material. In this step, the

metal oxide is reduced back to the pure metal or suboxide using the hydrocarbon as reducer in the second step of the reaction.

[0024] The two step reaction process provides two product streams, the first of which contains carbon dioxide and water, wherein the carbon dioxide and minor impurities can be collected and sequestered for storage. Thereby, CLC enables the generation of power. The CLC system is composed of two reactors, an air reactor and a fuel reactor. The fuel is introduced into the fuel reactor, which contains a metal oxide. In the most common process where methane is utilized, the exit gas stream from the fuel reactor contains CO_2 and H_2O . A stream of substantially pure CO_2 is obtained when H_2O is condensed. The reduced metal oxide is transferred to the air reactor where it is oxidized.

[0025] In one example of the prior art, a nickel-based system burning pure carbon would involve the two following redox reactions:



When reactions (1) and (2) are combined, the reaction set reduces to straight carbon oxidation with the nickel acting as a catalyst or oxygen carrier only:



[0026] In chemical looping combustion of the prior art, the CO_2 is inherently separated from other flue gas components, such as N_2 and O_2 and thus no energy is expended for the gas separation and no gas separation equipment is needed. Depending on the metal oxide and fuel used, reaction (1) is often exothermic, while reaction (2) is endothermic. The total amount of heat evolved from reactions (1) and (2) is the same as for common combustion processes where the oxygen is in contact with the fuel.

[0027] In 2001, a design based on the circulating fluidized bed principle was presented by Lyngfelt, Leckner and Mattisson. Most of the work so far in chemical looping combustion has been directed to applications that employ a dual fluidized bed system where the fluidized beds are interconnected. The metal oxide is in the form of particles employed as an oxygen carrier and bed material providing the oxygen for combustion in the fuel reactor. The reduced metal is then transferred to the second fluidized bed (air reactor) and re-oxidized before being reintroduced back to the fuel reactor completing the loop.

[0028] In the processes of the prior art, the metal oxide or metal suboxide is typically placed on a ceramic support material, for example NiAl_2O_4 , and this material is processed in dual fluid bed type reactor systems in a pelletized form. Besides nickel oxide, iron, manganese and copper oxides have been evaluated. For example, the National Energy Technology Laboratory carried out an evaluation of these metal oxides using a high-pressure flow reactor at 150 psi with synthesis gas and found that they showed a stable reactivity over three high-pressure cycles. The team concluded that though direct coal combustion is feasible with metal oxides, it would be necessary to develop an efficient solid circulation process and ash/metal-oxide separation process.

[0029] The prior art focuses on the development of suitable oxygen carrier supports or binders for the process. The ability of the oxygen carrier supports to convert a fuel gas fully to CO_2 and H_2O has been investigated thermodynamically. For example, U.S. patent application Ser. No. 11/010,648 to Tho-

mas et al. discloses a method for producing hydrogen gas which comprises reducing a metal oxide in a reduction reaction between a carbon-based fuel and a metal oxide to provide a reduced metal or metal oxide having a lower oxidation state, and oxidizing the reduced metal or metal oxide to produce hydrogen and a metal oxide having a higher oxidation state. The metal or metal oxide is provided in the form of a porous composite of a ceramic material containing the metal or metal oxide.

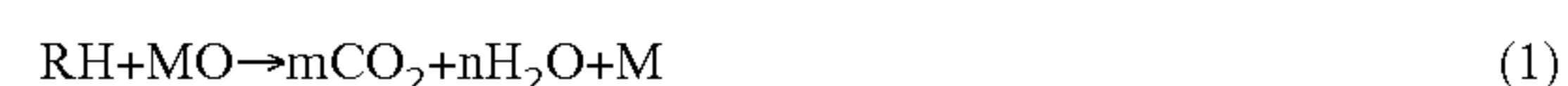
[0030] Many types of oxygen carrier supports or binders have been studied, including zirconia, alumina, metal aluminate spinels, titanium dioxide, silica, and kaolin clay. Yttriated zirconia remains the support considered to be the most efficient because it acts as an ion conductor for the O^{2-} ions at the working temperatures and thereby increases the reactivity of the redox system. A number of patents disclose cerine-zirconia type oxides in the field of the process using a redox active mass in a circulating bed process, including in chemical looping combustion.

[0031] A common problem with all transitional metal oxygen carriers is the formation of carbon deposits (i.e. coke) on the surfaces of carrier particles during the reduction phase. M. Ishida and H. Jin have reported that carbon deposits cause degradation of the physical strength of the particles and their chemical stability.

[0032] In conventional CLC, the bulk of the power is generated by the hot flue gas from the air reactor entering a gas turbine. Thus, a power plant's overall thermal efficiency is highly dependent on the maximum temperature that can be tolerated by the carrier during oxidation for extended periods. Sensitivity analysis shows that thermal efficiency varies with an increase in temperature of the reaction. It is currently thought that to achieve greater efficiencies, appropriate metal oxygen carrier supports are required.

[0033] The arrangement of a reversible CLC engine is based on receiving heat at high temperature from the exothermic oxidation reaction. Part of this energy can be converted into work; the rest is utilized as heat. Almost all of that heat can be absorbed by the endothermic reduction reaction. Therefore, this arrangement requires the redox reactions to be exothermic and endothermic respectively.

[0034] U.S. Pat. No. 5,447,024 to Ishida et al. discloses a chemical looping combustion system utilizing the following formulae (1) and (2).



The reduction product (M) of metallic oxide (MO) obtained according to formula (1) is utilized in the oxidation reaction of formula (2). Therefore, a chemical looping reaction occurs with MO as an oxygen carrier. The reaction of the formula (1) is an endothermic reaction of the metallic oxide (MO) and a fuel (RH) with low-energy absorption in a low-temperature region (about 600-1,000 K). The reaction of the second formula (2) is an exothermic oxidation reaction of the product (M) of the first step in a high-temperature region (about 800-1,700 K). A high-temperature exhaust gas is produced by the heat of the reaction and is utilized for driving a gas turbine. The product (M) is exemplified by metals such as iron, nickel, copper and manganese. The patented process uses circulating bed technology to allow continuous change of the active mass from the oxidized state to the reduced state.

[0035] The patent claims as the active mass the use of the redox pair NiO/Ni , alone or associated with binder YSZ (de-

finer by zirconia stabilized by yttrium). The advantage of the binder in the process is the increase of the mechanical strength of the particles. The particles would be too weak to be used in a circulating bed when NiO/Ni is used alone.

[0036] FIGS. 1 and 2, demonstrate the CLC process of the prior art utilizing NiO, Mn_3O_4 , Fe_2O_3 and other oxides. The figures demonstrate that reaction (2) is highly exothermic with adiabatic temperatures exceeding 3000°C . Such high temperatures make it difficult to control and maintain the temperature in the fluidized bed reactor below the melting point of either the metal oxide or the metal. In addition, in order to avoid forming sintered build-ups, good temperature control and cooling is required, lack of which in the prior art processes results in increased heat losses from the process. The endothermic step of these two reactions consumes substantial energy from the exothermic reaction step and this heat transfer cannot be realized with zero heat loss. As a result, the thermal efficiency of the chemical looping combustion processes of the prior art is poor and a process for improved thermal efficiency is needed.

[0037] Heat transfer and endothermicity of reaction are also substantial problems in various other industrial processes. In the industrial process known as steam reforming, hydrogen is produced by passing steam and a hydrocarbon through a nickel catalyst. Other processes include the gasification of biomass, the catalytic reforming of petroleum hydrocarbons, the decomposition of methanol. G. P. Curran, C. E. Fink, and E. Gorin in an article entitled CO_2 Acceptor Gasification Process, in Fuel Gasification, suggest the reaction: $\text{CO}_2 + \text{CaO} = \text{CaCO}_3$. The reaction is highly exothermic, thereby supplying the heat consumed by the endothermic gasification reaction. Furthermore, CO_2 and CO are in equilibrium via the water shift reaction: $\text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2$. Consequently, removing the CO_2 has the effect of also removing the CO, allowing the production of a gas containing a large mole fraction of hydrogen. The authors conclude, however, that for this process to be practical, it is necessary to reconvert the CaCO_3 back to CaO. The heat necessary to do this can be readily generated by burning some fuel; however, transferring the heat to where it is needed within the reactor system is a difficult and expensive problem. Thus, these processes of the prior art leave a need for a new method of burning fuel which allows for more effective energy generation, better heat transfer and reduced heat losses.

[0038] The majority of the work performed to date on chemical looping combustion has been performed using methane and coal as the fuels of choice. Current CLC processes operate most effectively with a gaseous fuel material such as methane. Solid fuel material CLC processing of coal is desirable but is less effective due to the restrictions of the solid to solid reactant mass transfer limitations of the process. In addition, when processing coal as the fuel material, the oxygen carrier becomes "poisoned" over time by the non-combustible mineral components contained in the coal, known as fly ash. This contamination affects the reactivity and porosity of the heterogeneous oxygen carrier system rendering the metal oxide and support ceramic unusable. When the oxygen carrier is depleted, the pelletized oxygen carrier material must be removed from the fluid bed reactor for reprocessing. At that point, the valuable metal oxide must be separated from the substrate or support ceramic. Rejuvenation of the metal oxide and separation and recovery of the

substrate ceramic waste components is a costly process which has an adverse impact on the overall cost of the CLC processes of the prior art.

[0039] Limited studies have been performed with oxygen carriers used to combust liquid fuels. The application for CLC for power production for liquid fuels such as heavy hydrocarbons is gaining wide interest in the oil and refining industry. The use of liquid fuels raises specific problems of implementation that are different than for gas or solids.

[0040] The largest, a 50 kW, chemical looping combustion system in operation as of 2008 was built in Korea and operated continuously for 25 hours. In Europe, current experience is from a 10 kW CLC facility located in Chalmers University of Technology in Sweden. The Technical University of Vienna in Austria is working on scaling-up its CLC process. These various CLC facilities implement the known developed variables and each process implements various trade-offs between efficiency, carbon dioxide capture and oxygen carrier properties.

[0041] Therefore, despite the progress in CLC technology, the world still desires an energy generation process that is highly efficient and can reduce the emission of unwanted side products while being economically practical to operate. The process and apparatus of the present invention take us one step closer to the desired solution.

[0042] The above and other features of the invention, including various novel details of construction and combination of parts, will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular reactions and apparatus embodying the invention are shown by way of illustration only and not as a limitation of the invention. The principles and features of the invention may be employed in various and numerous embodiments without departing from the scope of the invention.

SUMMARY OF THE INVENTION

[0043] An object of the present invention is the generation of useful work. The improvement over the prior art is that both reaction steps of the process are exothermic and useful work is generated during exothermic chemical looping combustion conditions in both reactions steps of the process. Embodiments of the present invention address the need for a high efficiency energy generation process by providing a process for chemical looping combustion comprising contacting a reduced oxygen carrier with oxygen to form an oxidized oxygen carrier, and contacting said oxidized oxygen carrier and a fuel to produce said reduced oxygen carrier and carbon dioxide, wherein both steps of the process are exothermic. During the process, the steps can be performed in either order within the furnace.

[0044] In accordance with one embodiment of the present invention, the process for chemical looping combustion is performed in a furnace and comprises a first step wherein a reduced oxygen carrier is contacted with oxygen to form an oxidized oxygen carrier, and a second step wherein an ash-containing fuel is contacted with said oxidized oxygen carrier to produce a reaction product comprising said reduced oxygen carrier, carbon dioxide and fly ash. Both the first step and the second step are exothermic.

[0045] One preferred embodiment of the present invention provides a process for chemical looping combustion in a flash furnace. The flash furnace comprises a first reactor and a second reactor receivably connected to the first reactor. The

process comprises the steps of: (a) feeding oxygen and a reduced oxygen carrier into the first reactor having a first reactor temperature at a location that is not a reaction zone, the oxygen and the reduced oxygen carrier each having a temperature that is lower than the first reactor temperature, and the first reactor temperature being sufficient to ignite the oxygen and the reduced oxygen carrier as they pass through the first reactor and create a reaction that is sufficiently exothermic to form a self-sustaining reaction zone having a first flash temperature, said reaction producing an oxidized oxygen carrier; (b) feeding the oxidized oxygen carrier and a fuel into the second reactor at a location that is not a reaction zone having a second reactor temperature, the oxidized oxygen carrier and fuel each having a temperature that is lower than the second reactor temperature, and the reactor temperature being sufficient to ignite the oxidized oxygen carrier and the fuel as they pass through the second reactor and create a reaction that is sufficiently exothermic to form a self-sustaining reaction zone having a second flash temperature, the reaction producing the reduced oxygen carrier and carbon dioxide; and (c) optionally, feeding the reduced oxygen carrier from the second reactor to the first reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] In order that the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended figures.

[0047] FIG. 1 is a graph showing the enthalpy change for reduction reactions with carbon.

[0048] FIG. 2 is a graph showing the enthalpy change for reduction reactions with methane.

[0049] FIG. 3 is a diagram flowsheet of the high thermal efficiency chemical looping combustion process of the present invention.

[0050] FIG. 4 is a graph showing the enthalpy change for reduction reactions with hydrogen.

[0051] FIG. 5 is a graph showing of the thermal decomposition of MoO_3 according to the process of the present invention.

[0052] FIG. 6 is a graph showing the equilibrium composition for the reduction of MoO_3 with a stoichiometric amount of carbon according to the process of the invention.

[0053] FIG. 7 is a graph showing the thermal decomposition of Na_2O_2 .

[0054] FIG. 8 is a graph showing the thermal decomposition of MnO_2 .

[0055] FIG. 9 is a graph showing the thermal decomposition of Rh_2O_3 .

[0056] FIG. 10 is a graph showing the thermal decomposition of PdO .

[0057] FIG. 11 is a graph showing the thermal decomposition of PtO .

[0058] FIG. 12 is a graph showing the thermal decomposition of NiO .

[0059] FIG. 13 is a graph showing the thermal decomposition of V_2O_5 .

[0060] FIG. 14 is a graph showing the thermal decomposition of TiO_3 .

[0061] FIG. 15 is a graph showing the thermal decomposition of OsO_4 .

[0062] FIG. 16 is a graph showing the thermal decomposition of Re_2O_7 .

[0063] FIG. 17 is a graph showing the thermal decomposition of Tc_2O_7 .

[0064] FIG. 18 is a graph showing the thermal decomposition of CuO .

[0065] FIG. 19 is a graph showing the thermal decomposition of BaO_2 .

[0066] FIG. 20 is a graph showing the equilibrium composition for the reduction of carbon dioxide with carbon.

DETAILED DESCRIPTION OF THE INVENTION

Furnaces

[0067] The process of the invention is particularly suited in the environment of chemical looping combustion systems. Without limiting the applicability of the invention, the invention will be specifically described in the environment of chemical looping combustion. The process of the current invention may be carried out in various types of combustion systems, including rotary kilns, multiple hearth furnaces, vertical tube furnaces or fluidized bed reactors.

[0068] With reference to FIG. 3, in a preferred embodiment, the process is carried out in a flash furnace. The flash furnace utilized for the process of the invention will contain at least two separate reaction vessels, herein referred to as “reactors”, though more reactors may be appended.

[0069] The temperature of one reactor may vary from the temperature of the second reactor. The term “reactor temperature” as used herein refers to the temperature of a reactor at any particular time at the location within the reactor where the reactants are being fed into the reactor. It is preferred that the reactants be fed into the reactor at the top of the furnace, such that the reactants fall gravitationally through the furnace and react with one another as they are falling. As the reagents begin and continue to react within the reactor, the temperature within the reactor will increase. The reactants will then enter the flash zone where the reaction will proceed to its completion.

[0070] Therefore, in a preferred embodiment of the process of the invention, the reduced oxygen carrier flows concurrently in the same direction with the flow of the oxygen in the first reactor. Similarly, in the second reactor of the furnace, the oxidized oxygen carrier flows concurrently in the same direction with the flow of the fuel. The concurrent flow of the process increases the contact time between the reactants, thereby increasing the kinetics of the reaction and ensuring completion of the reaction. Concurrent flow also enables control of the oxygen carrier to fuel ratio within the process thereby increasing the accuracy of the reagent ratio in the process of the invention.

Flash

[0071] Embodiments of the invention provide a high thermal efficiency CLC process wherein substantial energy is generated during both reaction steps of the process. Each reaction creates a sufficiently exothermic reaction having a stable flash reaction zone in which these reactions proceed to their completion. The term “flash” or “flash zone” will be used herein to refer to a reaction zone that is self-sustaining and has a high temperature as a result of the reactants coming into contact with one another in the reactor. As used herein, the term “flash temperature”, as distinguished from “reactor temperature”, refers to the highest temperature of the reaction in the flash zone of the reactor.

[0072] For practical purposes of operation of the flash furnace, it is preferred that the length of the reactor be sufficiently long to allow some differential between the reactor temperature and the flash temperature so that the reactants can have at least a few seconds to fall through the reactor before the flash is created within the reactor. In one embodiment of the process, the fuel and the oxidized oxygen carrier are blended prior to being passed into the second reactor. The blending can be carried out by various mixing or blending processes commonly known and commercially available for such industrial processes.

Continuous Process

[0073] The preferred process is continuous in that the reduced metal oxide or metal suboxide is recycled back in a loop into the system, hence the term “looping”. The oxygen carrier can be recycled in its’ heated state from the second reactor, which will further facilitate the formation of a stable flash in the reactor. In order to optimize the continuity of reaction, in a preferred embodiment, the oxygen and the reduced oxygen carrier are fed into the first reactor at a rate that is substantially constant while the first and the second reactor are, respectively, maintained at substantially constant temperatures.

Oxygen Carriers

[0074] The exothermic conditions of the process of the invention can be achieved by carefully choosing the appropriate oxygen carrier and unique operating conditions in a way that both reactions (1) and (2) become highly exothermic. By the term “reduced oxygen carrier” as used herein is meant a metal or a metal suboxide. The term “oxidized oxygen carrier” as used herein refers to an oxygen carrier that has been oxidized such that it has a higher oxidation state than the reduced oxygen carrier. The term “oxygen carrier” is used herein to refer to either reduced oxygen carrier or oxidized oxygen carrier.

[0075] The preferred reduced oxygen carriers of the invention are rhenium, platinum, rhodium, palladium, copper, barium, manganese, molybdenum, vanadium, bismuth, lead, mercury, sodium, potassium, rubidium, and cesium.

[0076] One embodiment of the invention is a process wherein more than one oxygen carrier is utilized at the same time within the furnace. A preferred embodiment of such a process is the combination of MoO_3 and Re_2O_7 .

[0077] In contrast to the prior art, the oxygen carrier within the process of the invention is substantially free-flowing. By “free-flowing”, it is meant that the oxygen carrier is not supported on a binder material of any sort, such as the ceramic supports of the prior art. When coal is reacted with a heterogeneous system, where the oxygen carrier is bound to a substrate, it becomes challenging to completely burn the fuel due to the difficulty in providing direct physical contact between the reagent particles.

[0078] In addition, virtually no vapor pressure is created over the oxygen carrier systems of the prior art, as can be seen for example in FIG. 12 for NiO in the temperature range of 100-1500° C. The oxidation reaction proceeds solely in a solid state. In the improved process of the invention, the free-flowing reactants flow co-currently while the oxygen carrier acting as oxidizing agent develops a tangible vapor pressure. The vapor greatly facilitates the mass transfer and kinetics and ultimately leads to complete fuel combustion.

Creating such unique kinetic conditions for the CLC process of the invention also leads to the removal of the volatile impurities, such as mercury, sulfur and others. Thus the CO_2 , SO_2 , and Hg are removed in highly concentrated form for capture and sequestration. It is also important to note that production and emission of nitrogen oxides are dramatically reduced during the fuel combustion process of the invention.

[0079] It is relevant to note that the nickel oxide used in the CLC processes of the prior art presents well-known serious health and environmental problems. Among the oxides that can be used in the improved CLC process of the present invention, lead, mercury and some other compounds present a clear hazard. Therefore, preferred are oxides and/or metals that do not present serious health problems. These are molybdenum, vanadium, bismuth, platinum, rhodium, and palladium oxides, though due to their high cost, platinum, rhodium and palladium are less preferred.

[0080] Preferably, the oxygen carrier particles used in the process of the invention are in powder form. By “powder” is meant a solid substance that is in a state of fine, loose particles. The powder form of the oxygen particles can be obtained by crushing, grinding, disintegration, or other mechanisms. Preferably, the oxygen carrier has a particle size of from 100 nanometers to 1 mm as determined by laser light scattering. More preferably, the oxygen carrier is in the form of a powder having a particle size of from 20 microns to 250 microns as determined by laser light scattering.

[0081] In order for the materials to be accepted for use in the CLC process of the invention, it is desirable that the oxide/suboxide or oxide/metal pairs meet the following criteria: (1) both reactions must be exothermic; (2) the reduced oxygen carrier must generate enough gaseous species to promote the oxidation of a solid fuel such as coal; and (3) the re-oxidation of the suboxide/metal with air at atmospheric pressure must be thermodynamically feasible.

[0082] Tables 11-13 of the Examples and FIGS. 7-19 reflect the correspondence of various oxide/suboxide and oxide/metal pairs that meet the outlined criteria of the invention. Various oxygen carriers can be chosen for reaction with fuel in the chemical looping combustion process of the invention. For example, rhenium (VII) oxide is a volatile compound and its reaction with fuel is exothermic (see Table 11).

[0083] It can be seen from FIGS. 14, 15 and 17 that the oxides of Tl, Os, and Tc become volatile at low temperatures which make them practically impossible for processing. On the contrary, the vanadium pentoxide (FIG. 15) is thermally quite stable and may be difficult to use for the oxidation of a solid fuel such as coal. For comparison, the nickel oxide (FIG. 13) normally used in the traditional CLC processes of the prior art exhibits the same thermal pattern.

Vaporization

[0084] In another embodiment of the invention, the oxygen carrier is at least partially vaporized in the furnace. In a process where coal is utilized as the fuel in the reaction, a substantial vapor phase in the reactor is important to create the exothermic reaction of the solid coal particulate in order to maintain the high-temperature flash conditions and the stability of the flash. The reactions can therefore be driven to their completion using near stoichiometric amounts of the reagents. On the contrary, carrying out the reduction of the metal oxides in either a rotary kiln or a fluidized bed reactor

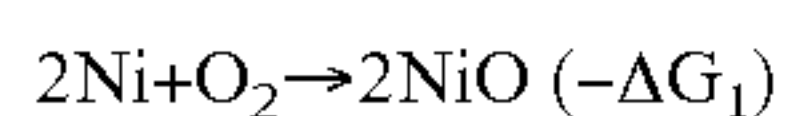
requires a large excess of one reagent and/or long retention time due to mass transfer limitations that make it difficult to achieve complete reaction.

[0085] Other embodiments of the invention include processes wherein the temperature within the first reactor is above the solid/liquid phase transition temperature of the reduced oxygen carrier; the temperature within the first reactor is above the solid/gas phase transition temperature of the reduced oxygen carrier; the temperature within the first reactor is above the liquid/gas phase transition temperature of the reduced oxygen carrier; the temperature within the second reactor is above the solid/liquid phase transition temperature of the oxidized oxygen carrier; the temperature within the second reactor is above the solid/gas phase transition temperature of the oxidized oxygen carrier; or the temperature within the second reactor is above the liquid/gas phase transition temperature of the oxidized oxygen carrier. Volatilization of the oxygen carrier reagents will create superior mass transfer of the oxygen carriers and promote the reaction kinetics. This advantage will promote the completion of the reactions while allowing for a reduction in the need for a large excess availability of the oxygen carrier materials. These phase changes can be identified by the change in enthalpy values, such as those set forth in the tables within the Examples of the invention hereinbelow.

[0086] In chemical looping combustion, isolation of the fuel from air simplifies the number of chemical reactions in combustion. According to a preferred embodiment of the process of the invention, employing oxygen in the oxygen carrier without nitrogen and the trace gases found in air will eliminate the primary source for the formation of nitrogen oxide (NO_x), producing an off gas composed primarily of carbon dioxide and water vapor. Such a rich gas stream high in CO_2 is a great advantage for carbon capture technologies.

Temperature Conditions

[0087] Using as an example a nickel-based system, burning pure carbon involves the following reactions, with ΔG signifying a change of Gibbs free energy:



[0088] According to the 1st and 2nd laws of thermodynamics, the maximum amount of work that a system can produce is equal to the change of free Gibbs energy for reaction (3)—($-\Delta G_3$). This statement is true provided thermodynamically reversible conditions exist for reactions (1) and (2). It is practically impossible to carry out the process at thermodynamic equilibrium at each given time/intermediate composition. Therefore, according to the 2nd law of thermodynamics, the actual amount of useful work will be always less than $-\Delta G_3$. As only one exothermic reaction is used to produce useful work in the chemical looping combustion processes of the prior art, the useful work of the prior art CLC processes cannot exceed $-\Delta G_2$. In order to get closer to thermodynamically reversible conditions and maximum useful work, the heat losses for reactions (1) and (2) should be minimized. In a preferred embodiment, the creation of adiabatic conditions (zero heat losses) within the reaction process would bring the theoretical temperature conditions of the reaction closer to thermodynamic reversibility.

[0089] In order to minimize heat losses, retention of temperature through “looping” of the oxygen carrier or preheating of the reagents will further promote stability of the flash in each reactor. Therefore, “looping” steps 1 and 2 will create an opportunity to charge heated metal oxides and suboxides or metals into the furnace further increasing the thermal efficiency of the system. Therefore, in a preferred embodiment of the process, the reactants can be preheated before being fed into the reactor, though preferably to a temperature that is lower than the flash temperature. Thus, the reduced oxygen carrier and the oxygen can be preheated before being fed into the first reactor of the furnace and the fuel and the oxidized oxygen carrier can be preheated before being fed into the second reactor of the furnace.

[0090] Carrying out the process at higher temperatures will greatly increase the rate and the completion of the reactions. This opportunity simply does not exist for the processing of NiO , Fe_2O_3 and Mn_3O_4 oxygen carriers utilized in the processes of the prior art as these first reactions are endothermic (see FIGS. 1 and 2).

[0091] Another means for controlling the temperature conditions within the furnace is by controlling the amount of reagent fed into the system. In a preferred embodiment, the reduced oxygen carrier and the oxygen are fed into the first reactor at a rate sufficient to substantially off-set the heat loss of the first reactor and create a flash; and the oxidized oxygen carrier and the fuel are fed into the second reactor at a rate sufficient to substantially off-set the heat loss from the second reactor and create a flash.

Residence Time

[0092] Due to the short residence time in the flash furnace, the oxygen carriers in either the first or the second step will have little or no time to agglomerate, and therefore, will have high surface area. Since the oxygen carriers will be free flowing and their bulk densities will be lower than those of agglomerated oxygen carriers. As a result, the residence time in the flash will increase and will work to drive the chemical reactions to their completion. In the preferred embodiment of the process under desired reaction conditions within a flash furnace, the process of the residence time of the oxygen and the reduced oxygen carrier in the first reactor being from 0.01 to 1.0 minute, and more preferably, from 0.01 to 10 seconds. Similarly, the residence time of the fuel and the oxidized oxygen carrier in the second reactor is from 0.01 seconds to 1.0 minute and preferably from 0.01 seconds to 10 seconds.

[0093] According to the invention, drastic reduction of the residence time and the oxygen carrier gas volume in the first step of the process will facilitate a dramatic reduction of the heat losses of the process in a flash furnace thereby allowing more energy to be converted into useful work.

Fuel

[0094] Many types of fuel can be utilized in the process of the invention, such as carbon, coal, hydrogen, hydrocarbon, biofuel, methane, natural gas, petroleum, crude oil, tar sands, oil shale, biomass, algae, fuel-rich waste gases from fuel cells and other fossil fuels and synthetic fuels. Various types of fuels may be combined during the process. Furthermore, the invention is not limited by the physical characteristics of the fuel being in a solid, liquid or gas phase, although embodiments having smaller particle sizes are preferred. It has been found that where the fuel is a carbon, a hydrocarbon, or

hydrogen, it can be fed into the process and apparatus of the invention in the form of a solid, a liquid or a gas.

[0095] For solid fuels, the process will be optimized if the fuel is fed into the reactor in a powder form. By “powder” as used herein is meant that a solid fuel source is first pulverized such that it creates free-flowing particles. In a preferred embodiment, the coal powder has a particle size of from 100 nanometers to 10 mm as determined by laser light scattering, and more preferably the coal powder has a particle size of from 20 microns to 250 microns as determined by laser light scattering. In one preferred embodiment of the process, particle size of the coal powder is substantially similar to the particle size of the oxygen carrier in order to optimize reaction kinetics.

Fly Ash

[0096] When a fuel that contains ash is utilized in the process, fly ash is produced during the process. As used herein, the term “fly ash” refers to non-combustible mineral components in the off-gas stream of the process. The fly ash produced from the burning of pulverized coal in a typical coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, bag-houses, or mechanical collection devices such as cyclones. The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. There are four main types, or ranks, of coal, each of which varies in terms of its heating value, its chemical composition, ash content, and geological origin. In addition to coal, ash-containing fuels include crude oil, tar sands, oil shale and natural gas.

[0097] Dealing with fly ash is a major obstacle to overcome when burning coal. The fly ash accumulates over time on the surface of the oxygen carrier causing the oxygen carrier to lose its effectiveness. Eventually, the oxygen carrier becomes unusable for further processing because it becomes practically impossible to either oxidize or reduce the compound.

[0098] Therefore, the oxygen carrier should be constantly or periodically removed from the reaction and the reaction compensated with pure oxygen carrier at the same time to avoid deleterious level of contamination. In one embodiment of the process of the invention, the reduced oxygen carrier and the fly ash are continuously removed from the furnace. Continuous removal of fly ash keeps the furnace free of build up and maintains the integrity of the process. In order to keep the process in continuous looping, substantially the same amount of reduced oxygen carrier that is removed from the furnace is fed back into the furnace, thereby maintaining the same reaction rates and flash temperatures within the reactors.

[0099] In traditional CLC processes, the material contaminated with fly ash is either considered a loss or requires costly re-processing to separate the metal or metal oxide from the support material and recover the valuable metal components. In the process of the invention, especially when processing oxides of molybdenum and vanadium, the material removed from the furnace is a mixture of fly ash together with the reduced oxygen carrier. The removed material can be utilized as an alloy additive in steel or ferroalloy production, particularly in a process to produce an alloy material containing iron and slag, including ferroalloys such as ferrovandium, ferromolybdenum and ferromanganese. Since the oxygen carrier is a homogeneous free-flowing material without any binder or substrate support, no separation step is required. Taking out

the homogeneous free-flowing oxygen carrier in a suboxide form for direct sale will also result in a reduced reagent usage in the alloy production field. As a result, coal combustion via the improved CLC process of the invention will become even more economically attractive as compared to prior art processes having supported oxygen carrier systems.

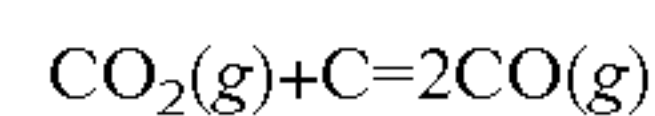
Carbon Dioxide and Carbon Monoxide

[0100] The gaseous products of the combustion process of the invention will be comprised of CO₂, CO and H₂O. Carbon monoxide is a chemically reactive gas that can be used for the production of a variety of chemicals, like metal carbonyls, phosgene and array of organic compounds such as methanol and other alcohols, formic and other organic acids, and their derivatives. According to an embodiment of the invention, the carbon monoxide can be separated and carbon dioxide can be substantially separated, captured and sequestered.

[0101] The prior art fluidized bed technology is well known for generating large amounts of dust during the combustion process. The off-stream of the endothermic reaction is comprised not only of CO₂ but also of tangible amounts of carbon. Excess amounts of carbon are required by the processes of the prior art at least in part due to their use of supported oxygen carriers of undetermined particle sizes. As shown in FIG. 20, as the temperature of the off-gas of the reaction changes, the CO₂ and carbon do not remain chemically inert to each other, and consequently a small amount react to generate an appreciable amount of CO. The amount of CO cannot be controlled nor calculated because the temperature of the off-stream gas is unstable. As a result, the presence of CO within the CO₂ stream, especially in unknown ratios, presents a challenge for the separation and sequestration of carbon dioxide. High CO levels may be desired for production of carbon containing chemicals. CO can be desired over CO₂ due to its significantly higher chemical reactivity.

[0102] In one embodiment of the invention, in order to produce a substantially pure stream of CO₂ during the process of the invention, the fuel and the oxidized oxygen carrier are fed into the second reactor in substantially stoichiometric amounts in order to produce an excess of carbon dioxide over carbon monoxide. In a process where the fuel and the oxidized oxygen carrier are fed into the second reactor in less than stoichiometric amounts, larger quantities of carbon monoxide will be produced.

[0103] It has also been discovered herein that another means of controlling the production of CO₂ and CO involves the use of the following chemical reaction:



$$K = (\text{P}_{\text{CO}})^2 / (\text{P}_{\text{CO}_2})$$

wherein K is the equilibrium constant at a given temperature and K is a function of temperature solely and P is the partial pressure of the corresponding gaseous species (CO and CO₂ respectively). Adding CO₂ gas to the system at a given temperature will cause an increase in the partial pressure of CO according to the above equation for the equilibrium constant. In the event that the CO₂ gas is injected into the furnace at the location of the flash, wherein the CO₂ gas has a temperature significantly lower than the flash temperature, the temperature of the flash will be decreased. This will cause a change in the equilibrium constant. As a result, the partial pressure of CO may decrease (depending on the decrease of temperature.) Therefore, the amount of CO produced can be con-

trolled not only by the partial pressure of the CO₂ gas in the flash zone but also by the flash temperature which can be changed by the amount of the CO₂ gas added to the flash zone. In this manner, it is hereby possible to control the CO₂/CO ratio and production of the CO₂ and CO.

EXAMPLES

[0104] The following examples illustrate the process and are intended to be purely exemplary of the use of the invention and should not be viewed as limiting its scope. In the tables below, T (in degrees Celsius) indicates the reaction or reactor temperature within the furnace. ΔH indicates the enthalpy change of the reaction, ΔS is the entropy change of the reaction and ΔG is the change in Gibbs free energy. K is the equilibrium constant of the reaction at the given temperature. The values of the examples were calculated using HSC CHEMISTRY® for Windows Thermodynamic Software by Outokumpu Research Oy of Finland.

[0105] Negative ΔG values in the tables below signify that the equilibrium of the reaction is shifted toward the right, i.e. toward formation of the products. The greater the value of the negative ΔG, the more complete the reaction, such that there would be an insignificant amount of reactants left in the product of the reaction, which is also indicated by the extremely high K values. The negative ΔH values in the tables indicate that the reactions are exothermic.

Example 1

[0106] Molybdenum was used as the metal and reacted with oxygen to form molybdenum trioxide as the oxidized oxygen carrier. Table 1 demonstrates the thermodynamic analyses of the chemical looping combustion process of the invention using molybdenum trioxide with the following combustion reaction: $2\text{MoO}_3 + \text{C} = 2\text{MoO}_2 + \text{CO}_2(\text{g})$

TABLE 1

T C	ΔH kcal	ΔS cal/K	ΔG kcal	K
100.000	-19.277	34.432	-32.126	6.565E+018
200.000	-19.412	34.113	-35.552	2.649E+016
300.000	-19.577	33.797	-38.948	7.124E+014
400.000	-19.802	33.437	-42.310	5.469E+013
500.000	-20.095	33.033	-45.634	7.956E+012
600.000	-20.453	32.597	-48.916	1.757E+012
700.000	-20.877	32.139	-52.153	5.169E+011
800.000	-21.360	31.667	-55.343	1.870E+011
900.000	-45.876	8.910	-56.329	3.122E+010
1000.000	-47.006	7.984	-57.172	6.531E+009
1100.000	-48.010	7.225	-57.931	1.663E+009
1200.000	-48.880	6.613	-58.622	4.984E+008
1300.000	-49.609	6.134	-59.258	1.710E+008
1400.000	-50.190	5.775	-59.852	6.587E+007
1500.000	-50.616	5.527	-60.417	2.801E+007

Example 2

[0107] Vanadium pentoxide was used as the reduced oxygen carrier and reacted with oxygen as follows: $\text{V}_2\text{O}_5 + \text{C} = \text{V}_2\text{O}_3 + \text{CO}_2(\text{g})$. Table 2 demonstrates the thermodynamic analyses of the CLC process of the invention using vanadium pentoxide.

TABLE 2

T C	ΔH kcal	ΔS cal/K	ΔG kcal	K
100.000	-14.618	42.080	-30.320	5.746E+017
200.000	-14.573	42.187	-34.533	8.963E+015
300.000	-14.553	42.227	-38.755	6.011E+014
400.000	-14.587	42.172	-42.976	8.994E+013
500.000	-14.710	42.005	-47.186	2.184E+013
600.000	-14.957	41.706	-51.372	7.237E+012
700.000	-30.684	25.207	-55.215	2.518E+012
800.000	-31.253	24.651	-57.707	5.664E+011
900.000	-31.786	24.175	-60.147	1.607E+011
1000.000	-32.284	23.768	-62.544	5.461E+010
1100.000	-32.744	23.420	-64.903	2.142E+010
1200.000	-33.165	23.124	-67.230	9.435E+009
1300.000	-33.543	22.875	-69.529	4.573E+009
1400.000	-33.874	22.671	-71.806	2.400E+009
1500.000	-34.156	22.507	-74.065	1.348E+009

Example 3

[0108] Table 3 sets forth the thermodynamic analyses of methane gas using molybdenum trioxide as the reduced oxygen carrier with the following reaction formula: $4\text{MoO}_3 + \text{CH}_4(\text{g}) = 4\text{MoO}_2 + \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

TABLE 3

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-176.034	279.607	-280.370	1.780E+039
200.000	-176.182	279.264	-308.316	1.097E+034
300.000	-176.765	278.165	-336.196	4.387E+030
400.000	-178.059	276.101	-363.917	1.743E+028
500.000	-180.146	273.224	-391.389	2.785E+026
600.000	-183.023	269.734	-418.541	1.098E+025
700.000	-186.645	265.814	-445.321	8.035E+023
800.000	-190.942	261.616	-471.695	9.147E+022
900.000	-396.477	70.843	-479.586	2.267E+021
1000.000	-406.413	62.709	-486.251	8.944E+019
1100.000	-415.364	55.936	-492.173	5.295E+018
1200.000	-423.266	50.377	-497.479	4.375E+017
1300.000	-430.045	45.920	-502.285	4.778E+016
1400.000	-435.631	42.474	-506.697	6.608E+015
1500.000	-439.948	39.964	-510.811	1.120E+015

Example 4

[0109] Table 4 sets forth the thermodynamic analyses of methane using vanadium pentoxide having the following reaction: $2\text{V}_2\text{O}_5 + \text{CH}_4(\text{g}) = 2\text{V}_2\text{O}_3 + \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

TABLE 4

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-137.042	343.602	-265.257	1.363E+037
200.000	-135.690	346.825	-299.790	1.256E+033
300.000	-134.720	348.700	-334.577	3.123E+030
400.000	-134.418	349.203	-369.484	4.714E+028
500.000	-135.085	348.297	-404.371	2.099E+027
600.000	-137.027	345.953	-439.095	1.863E+026
700.000	-268.714	207.807	-470.942	1.907E+025
800.000	-273.724	202.905	-491.472	8.394E+023
900.000	-278.571	198.586	-511.542	6.003E+022
1000.000	-283.213	194.788	-531.207	6.253E+021
1100.000	-287.622	191.452	-550.515	8.777E+020

TABLE 4-continued

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
1200.000	-291.765	188.539	-569.511	1.568E+020
1300.000	-295.604	186.016	-588.236	3.415E+019
1400.000	-299.099	183.861	-606.727	8.774E+018
1500.000	-302.207	182.056	-625.020	2.593E+018

Example 5

[0110] Table 5 sets forth the thermodynamic analyses of hydrogen utilizing molybdenum trioxide in the following combustion reaction: $\text{MoO}_3 + \text{H}_2(\text{g}) = \text{MoO}_2 + \text{H}_2\text{O}(\text{g})$

TABLE 5

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-86.121	24.017	-95.083	2.047E+013
200.000	-87.311	21.189	-97.336	5.580E+010
300.000	-88.498	18.914	-99.339	1.133E+009
400.000	-89.745	16.910	-101.128	7.046E+007
500.000	-91.073	15.072	-102.726	8.726E+006
600.000	-92.482	13.359	-104.147	1.702E+006
700.000	-93.966	11.751	-105.401	4.550E+005
800.000	-95.510	10.241	-106.500	1.528E+005
900.000	-147.260	-37.779	-102.939	3.835E+004
1000.000	-150.014	-40.034	-99.045	1.159E+004
1100.000	-152.436	-41.867	-94.946	4.093E+003
1200.000	-154.520	-43.333	-90.684	1.643E+003
1300.000	-156.254	-44.474	-86.291	7.335E+002
1400.000	-157.630	-45.322	-81.799	3.580E+002
1500.000	-158.633	-45.906	-77.235	1.886E+002

Example 6

[0111] Table 6 sets forth the thermodynamic analyses of hydrogen utilizing and vanadium pentoxide in the following reaction: $\text{V}_2\text{O}_5 + 2\text{H}_2(\text{g}) = \text{V}_2\text{O}_3 + 2\text{H}_2\text{O}(\text{g})$

TABLE 6

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-152.746	80.031	-182.609	3.667E+025
200.000	-154.375	76.159	-190.410	1.053E+021
300.000	-155.973	73.096	-197.868	1.082E+018
400.000	-157.670	70.370	-205.040	8.164E+015
500.000	-159.616	67.680	-211.943	2.090E+014
600.000	-161.967	64.827	-218.570	1.193E+013
700.000	-228.966	-5.501	-223.613	1.008E+012
800.000	-232.412	-8.874	-222.889	7.077E+010
900.000	-235.567	-11.687	-221.856	7.569E+009
1000.000	-238.427	-14.028	-220.567	1.122E+009
1100.000	-241.001	-15.976	-219.064	2.157E+008
1200.000	-243.289	-17.585	-217.383	5.112E+007
1300.000	-245.288	-18.899	-215.557	1.439E+007
1400.000	-246.993	-19.951	-213.612	4.671E+006
1500.000	-248.395	-20.765	-211.574	1.711E+006

[0112] Tables 1 through 6 demonstrate that the reactions of the process of the invention are thermodynamically favorable over a wide range of temperatures as indicated by the negative ΔG values. The negative ΔH values show that the reactions are exothermic.

[0113] Reactions taking place during the first step of the process are complex and sometimes cannot be described with one reaction in such a wide temperature range (Tables 1-4). For example, at high temperatures, carbon monoxide will evolve as one of the products when reducing molybdenum trioxide. Equilibrium composition for the reduction of MoO_3 with carbon as a function of temperature is shown in FIG. 6. It can be seen from FIG. 6 that only up to 800° C. of the equilibrium composition is described by the reaction shown in Table 1. Above that temperature, the CO content becomes tangible. It reaches almost 20% at 1500° C.

Example 7

[0114] Re-oxidation of the metal suboxides/metals is as critical as the oxidation of the fuel. The re-oxidation will be carried out in air, so the oxygen potential in air (2.1 E-01 atm) must be greater than the equilibrium partial pressure of oxygen for the corresponding re-oxidation reaction. The temperature ranges in which the oxygen potential in air is greater than that of the re-oxidation reaction can be calculated.

[0115] The equilibrium partial pressure of oxygen as a function of temperature for the re-oxidation reaction of bismuth is given in Table 7. The K column represents the oxygen pressure. It can be seen from Table 7 that the temperature range in which bismuth can be re-oxidized with air is approximately 100° C.-1500° C. in the reaction $0.667\text{Bi}_2\text{O}_3 = 1.333\text{Bi} + \text{O}_2(\text{g})$.

TABLE 7

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	384.602	178.070	318.155	2.884E-045
200.000	383.379	175.165	300.500	6.648E-034
300.000	397.339	200.706	282.304	1.861E-026
400.000	396.042	198.628	262.336	4.383E-021
500.000	394.440	196.413	242.583	4.069E-017
600.000	392.541	194.107	223.056	4.518E-014
700.000	390.344	191.729	203.764	1.153E-011
800.000	367.765	169.272	186.111	8.719E-010
900.000	352.523	155.524	170.070	2.673E-008
1000.000	346.251	150.393	154.778	4.459E-007
1100.000	340.010	145.674	139.977	4.729E-006
1200.000	333.797	141.307	125.631	3.508E-005
1300.000	327.612	137.244	111.706	1.953E-004
1400.000	321.452	133.448	98.173	8.607E-004
1500.000	315.316	129.886	85.009	3.130E-003

Example 8

[0116] Table 8 sets forth the temperature ranges calculated for the re-oxidation reactions listed in column 1 of the table according to the same analysis carried out for bismuth in Example 7.

TABLE 8

Reaction	Temperature Range (° C.)
$2\text{Na}_2\text{O} + \text{O}_2 = 2\text{Na}_2\text{O}_2$	100-1000
$2\text{K}_2\text{O} + \text{O}_2 = 2\text{K}_2\text{O}_2$	100-1200
$2\text{Rb}_2\text{O} + \text{O}_2 = 2\text{Rb}_2\text{O}_2$	100-700
$2\text{Cs}_2\text{O} + \text{O}_2 = 2\text{Cs}_2\text{O}_2$	100-900
$2\text{BaO} + \text{O}_2 = 2\text{BaO}_2$	100-700
$2\text{MnO} + \text{O}_2 = 2\text{MnO}_2$	100-900
$4\text{TcO}_2 + 3\text{O}_2 = 2\text{Tc}_2\text{O}_7$	100-1500

TABLE 8-continued

Reaction	Temperature Range (° C.)
$4\text{ReO}_2 + 3\text{O}_2 = 2\text{Re}_2\text{O}_7$	100-1500
$\text{OsO}_2 + \text{O}_2 = \text{OsO}_4$	100-1500
$\text{Rh}_2\text{O} + \text{O}_2 = \text{Rh}_2\text{O}_3$	100-800
$2\text{Pt} + \text{O}_2 = 2\text{PtO}$	100-500
$2\text{Pd} + \text{O}_2 = 2\text{PdO}$	100-700
$2\text{Cu} + \text{O}_2 = 2\text{CuO}$	100-1400
$2\text{Hg} + \text{O}_2 = 2\text{HgO}$	100-500
$\text{Ti}_2\text{O} + \text{O}_2 = \text{Ti}_2\text{O}_3$	100-700
$\text{MoO}_2 + \text{O}_2 = \text{MoO}_3$	100-1500
$\text{V}_2\text{O}_3 + \text{O}_2 = \text{V}_2\text{O}_5$	100-1500
$\text{Pb} + \text{O}_2 = \text{PbO}_2$	100-1100
$4\text{Bi} + 3\text{O}_2 = 2\text{Bi}_2\text{O}_3$	100-1500

Example 9

[0117] In reference to the example systems, metal suboxides and/or metals produced in the first step of the process, will be re-oxidized in the second step according to the reactions shown in Tables 9 and 10. Table 8 is a combustion reaction utilizing molybdenum trioxide with the formula $2\text{MoO}_2 + \text{O}_2(\text{g}) = 2\text{MoO}_3$.

TABLE 9

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-312.890	-141.309	-260.160	2.637E+036
200.000	-312.395	-140.133	-246.091	1.480E+027
300.000	-311.826	-139.046	-232.132	1.437E+021
400.000	-311.057	-137.814	-218.287	8.708E+016
500.000	-310.037	-136.407	-204.575	6.643E+013
600.000	-308.749	-134.843	-191.011	2.678E+011
700.000	-307.193	-133.158	-177.610	3.421E+009
800.000	-305.381	-131.388	-164.382	1.004E+008
900.000	-203.013	-36.357	-160.361	1.383E+007
1000.000	-198.490	-32.654	-156.917	2.745E+006
1100.000	-194.498	-29.633	-153.808	7.101E+005
1200.000	-191.067	-27.219	-150.970	2.257E+005

Example 10

[0118] Table 9 is a combustion reaction utilizing vanadium pentoxide with the formula: $\text{V}_2\text{O}_3 + \text{O}_2(\text{g}) = \text{V}_2\text{O}_5$.

TABLE 10

T C	ΔH kJ	ΔS J/K	ΔG kJ	K
100.000	-332.386	-173.307	-267.717	3.013E+037
200.000	-332.641	-173.913	-250.354	4.374E+027
300.000	-332.849	-174.314	-232.941	1.703E+021
400.000	-332.877	-174.365	-215.503	5.295E+016
500.000	-332.568	-173.943	-198.084	2.420E+013
600.000	-331.747	-172.953	-180.734	6.501E+010
700.000	-266.158	-104.155	-164.800	7.023E+008
800.000	-263.989	-102.032	-154.494	3.315E+007
900.000	-261.966	-100.228	-144.383	2.687E+006
1000.000	-260.090	-98.693	-134.439	3.283E+005
1100.000	-258.370	-97.391	-124.637	5.515E+004
1200.000	-256.817	-96.299	-114.954	1.192E+004
1300.000	-255.447	-95.399	-105.370	3.155E+003
1400.000	-254.277	-94.677	-95.868	9.844E+002
1500.000	-253.323	-94.123	-86.429	3.518E+002

[0119] The data shown in Tables 8-10 demonstrate that oxidation of the metal suboxides/metals with oxygen according to the process of the invention can be carried out in a flash furnace. The flash furnace will allow operation of the process at temperatures higher than those of fluidized bed or rotary kiln furnaces. Running the process at high temperature will significantly increase the rate of the chemical reaction and, therefore, the process throughput. The flash temperatures can be controlled by modifying the reactor temperatures.

Examples 11 and 12

[0120] Examples 11 and 12 demonstrate that the oxygen carriers in the process of the invention do not have to be completely cooled down to room temperature after the reduction or oxidation. According to the invention, they can be fed preheated into the next step of the reaction. This will facilitate the formation of a stronger sustainable flash and increase the overall thermal efficiency of the process as a result of reduced heat losses. The initial temperature of the oxygen carriers for steps 1 and 2 was assumed to be 400° C. This temperature was used to calculate the flash temperatures for the oxygen carriers, which are set forth in Tables 10 and 11. Tables 11 and 12 demonstrate that both reactions of the process are exothermic and the heat energy released is sufficient to create a stable flash.

TABLE 11

Reaction	Reactor Temperature (° C.)	Flash Temperature (° C.)
$\text{CH}_4 + 4\text{Na}_2\text{O}_2 = \text{CO}_2 + 4\text{Na}_2\text{O} + 2\text{H}_2\text{O}$	400	1071
$\text{CH}_4 + 4\text{K}_2\text{O}_2 = \text{CO}_2 + 4\text{K}_2\text{O} + 2\text{H}_2\text{O}$	400	740
$\text{CH}_4 + 4\text{Rb}_2\text{O}_2 = \text{CO}_2 + 4\text{Rb}_2\text{O} + 2\text{H}_2\text{O}$	400	1163
$\text{CH}_4 + 4\text{Cs}_2\text{O}_2 = \text{CO}_2 + 4\text{Cs}_2\text{O} + 2\text{H}_2\text{O}$	400	1032
$\text{H}_2 + \text{BaO}_2 = \text{BaO} + \text{H}_2\text{O}$	400	1834
$\text{CH}_4 + 4\text{MnO}_2 = 4\text{MnO} + \text{CO}_2 + 2\text{H}_2\text{O}$	400	1073
$1.5\text{C} + \text{Tc}_2\text{O}_7 = 2\text{TcO}_2 + 1.5\text{CO}_2$	400	2134
$1.5\text{C} + \text{Re}_2\text{O}_7 = 2\text{ReO}_2 + 1.5\text{CO}_2$	400	1521
$\text{C} + \text{OsO}_4 = \text{OsO}_2 + \text{CO}_2$	400	2499
$\text{C} + \text{Rh}_2\text{O}_3 = \text{Rh}_2\text{O} + \text{CO}_2$	400	1266
$\text{C} + 2\text{PtO} = 2\text{Pt} + \text{CO}_2$	400	2093
$4\text{PdO} + \text{CH}_4 = 4\text{Pd} + \text{CO}_2 + 2\text{H}_2\text{O}$	400	1555
$\text{C} + 2\text{CuO} = 2\text{Cu} + \text{CO}_2$	400	1085
$\text{C} + 2\text{HgO} = 2\text{Hg} + \text{CO}_2$	400	2199
$\text{C} + \text{Ti}_2\text{O}_3 = \text{Ti}_2\text{O} + \text{CO}_2$	400	1282
$\text{C} + \text{PbO}_2 = \text{Pb} + \text{CO}_2$	400	1632
$\text{C} + 2\text{MoO}_3 = \text{CO}_2(\text{g}) + 2\text{MoO}_2$	400	771
$\text{C} + \text{V}_2\text{O}_5 = \text{CO}_2(\text{g}) + \text{V}_2\text{O}_3$	400	705
$1.5\text{C} + \text{Bi}_2\text{O}_3 = 2\text{Bi} + 1.5\text{CO}_2$	400	318

TABLE 12

Reaction	Reactor Temperature (° C.)	Flash Temperature (° C.)
$2\text{Na}_2\text{O} + \text{O}_2 = 2\text{Na}_2\text{O}_2$	400	917
$2\text{K}_2\text{O} + \text{O}_2 = 2\text{K}_2\text{O}_2$	400	1254
$2\text{Rb}_2\text{O} + \text{O}_2 = 2\text{Rb}_2\text{O}_2$	400	767
$2\text{Cs}_2\text{O} + \text{O}_2 = 2\text{Cs}_2\text{O}_2$	400	909
$2\text{BaO} + \text{O}_2 = 2\text{BaO}_2$	400	1225
$2\text{MnO} + \text{O}_2 = 2\text{MnO}_2$	400	1994
$4\text{TcO}_2 + 3\text{O}_2 = 2\text{Tc}_2\text{O}_7$	400	876
$4\text{ReO}_2 + 3\text{O}_2 = 2\text{Re}_2\text{O}_7$	400	1439
$\text{OsO}_2 + \text{O}_2 = \text{OsO}_4$	400	721
$\text{Rh}_2\text{O} + \text{O}_2 = \text{Rh}_2\text{O}_3$	400	1870
$2\text{Pt} + \text{O}_2 = 2\text{PtO}$	400	1316
$2\text{Pd} + \text{O}_2 = 2\text{PdO}$	400	1944

TABLE 12-continued

Reaction	Reactor Temperature (° C.)	Flash Temperature (° C.)
$2\text{Cu} + \text{O}_2 = 2\text{CuO}$	400	2008
$2\text{Hg} + \text{O}_2 = 2\text{HgO}$	400	1675
$\text{Ti}_2\text{O} + \text{O}_2 = \text{Ti}_2\text{O}_3$	400	1413
$2\text{MoO}_2 + \text{O}_2 = 2\text{MoO}_3$	400	1272
$\text{V}_2\text{O}_3 + \text{O}_2 = \text{V}_2\text{O}_5$	400	1779
$\text{Pb} + \text{O}_2 = \text{PbO}_2$	400	>3000
$4\text{Bi} + 3\text{O}_2 = 2\text{Bi}_2\text{O}_3$	400	3166

Example 13

[0121] It was calculated that when carbon is heated with molybdenum oxide to 850° C., the flash temperature of the products will reach 1628° C. At temperatures above 700° C., molybdenum trioxide exhibits a tangible vapor pressure of various gaseous species (see FIG. 5). The existence of a gaseous metal oxide oxygen carrier species radically improves the mass transfer capability of this system improving the reaction rate kinetics and reaction completion. It can be seen from FIG. 5 that molybdenum trioxide creates tangible amounts of gaseous species during its decomposition at high temperatures; therefore, the fuel combustion reaction with MoO_3 at those temperatures will proceed mostly in the gaseous state.

Example 14

[0122] It was calculated that when methane is heated with molybdenum oxide to 850° C., the flash temperature of the products will reach 1600° C. When the reducing agent is also in the vapor phase, such as methane, the reaction will proceed very quickly to its full completion.

Examples 15 and 16

[0123] For the combustion of carbon and methane with vanadium pentoxide as the oxygen carrier, heating of the reagents to 700° C. leads to flash temperatures of 1371° C. and 1361° C., respectively. The release of energy during the process of the examples can be used to bring the fuel combustion processes to higher temperatures to form a stable flash. The enthalpy change steeply increases (~100%) at 900° C. for the combustion of fuel with molybdenum trioxide and at 700° C. for the combustion of fuel with vanadium pentoxide. These steep enthalpy changes are demonstrated in FIGS. 1, 2 and 4.

[0124] It will be apparent to those skilled in the art that various changes may be made without departing from the scope of the invention which is not considered limited to the specific embodiments described in the specification and drawings, but is only limited by the scope of the appended claims.

What is claimed is:

1. A process for chemical looping combustion comprising:
 - (a) contacting a reduced oxygen carrier with oxygen to form an oxidized oxygen carrier, and
 - (b) contacting said oxidized oxygen carrier and a fuel to produce said reduced oxygen carrier and carbon dioxide,
 wherein both steps are exothermic.

2. A process for chemical looping combustion in a furnace comprising:

- (a) a first step wherein a reduced oxygen carrier is contacted with oxygen to form an oxidized oxygen carrier, and
 - (b) a second step wherein an ash-containing fuel is contacted with said oxidized oxygen carrier to produce a reaction product comprising said reduced oxygen carrier, carbon dioxide and fly ash,
- wherein both the first step and the second step are exothermic.

3. A process for chemical looping combustion comprising the steps of:

- (c) contacting at least one reduced oxygen carrier with oxygen in a first reactor to form at least one oxidized oxygen carrier,
 - (d) passing the at least one oxidized oxygen carrier from said first reactor to a second reactor receivably connected to said first reactor,
 - (e) contacting said at least one oxidized oxygen carrier with at least one fuel in said second reactor to produce said at least one reduced oxygen carrier and carbon dioxide, and
 - (f) passing said at least one reduced oxygen carrier from said second reactor to said first reactor,
- wherein both reaction steps are exothermic.

4. A process for chemical looping combustion in a flash furnace, said flash furnace comprising a first reactor and a second reactor receivably connected to said first reactor, said process comprising the steps of:

- (a) feeding oxygen and a reduced oxygen carrier into the first reactor having a first reactor temperature at a location that is not a reaction zone, said oxygen and said reduced oxygen carrier each having a temperature that is lower than said first reactor temperature, and said first reactor temperature being sufficient to ignite the oxygen and the reduced oxygen carrier as they pass through the first reactor and create a reaction that is sufficiently exothermic to form a self-sustaining reaction zone having a first flash temperature, said reaction producing an oxidized oxygen carrier;
- (b) feeding said oxidized oxygen carrier and a fuel into said second reactor at a location that is not a reaction zone having a second reactor temperature, said oxidized oxygen carrier and said fuel each having a temperature that is lower than said second reactor temperature, and said reactor temperature being sufficient to ignite the oxidized oxygen carrier and the fuel as they pass through the second reactor and create a reaction that is sufficiently exothermic to form a self-sustaining reaction zone having a second flash temperature, said reaction producing the reduced oxygen carrier and carbon dioxide; and
- (c) optionally, feeding said reduced oxygen carrier from said second reactor to said first reactor.

5. A process for chemical looping combustion comprising the steps of:

- (g) feeding a reduced oxygen carrier and oxygen into a first reactor;
- (h) contacting the reduced oxygen carrier with the oxygen source in said first reactor to form an oxidized oxygen carrier;

- (i) passing the oxidized oxygen carrier from said first reactor to a second reactor receivably connected to said first reactor;
 - (j) feeding a fuel into said second reactor for contact with said oxidized oxygen carrier within said second reactor to produce a reaction product comprising said reduced oxygen carrier, carbon dioxide and carbon monoxide; and
 - (k) passing said reduced oxygen carrier from said second reactor to said first reactor;
- wherein the reaction in the first reactor and the reaction in the second reactor are both exothermic.
6. The process of claim 4 wherein the fuel is an ash-containing fuel and wherein the reaction in the second reactor further produces fly ash.
7. The process of claim 4 wherein the reduced oxygen carrier and the oxygen are preheated before being fed into the first reactor of the furnace.
8. The process of claim 4 wherein the fuel and the oxidized oxygen carrier are preheated before being fed into the second reactor of the furnace.
9. The process of claim 3 wherein the oxygen and the reduced oxygen carrier are fed into the first reactor at a rate that is substantially constant and the first reactor temperature and the second reactor temperature remain substantially constant.
10. The process of claim 4, wherein after step (b), the fuel and the oxidized oxygen carrier are blended prior to being passed into the second reactor.
11. The process of claim 1 or claim 2 wherein said process is performed in a flash furnace.
12. The process of claim 1 wherein said process is performed in a rotary kiln, a multiple hearth furnace, a vertical tube furnace or a fluidized bed reactor.
13. The process of claim 1 wherein said process is continuous.
14. The process of claim 1 further comprising recycling the reduced oxygen carrier produced during said second step into said first step of the process.
15. The process of claim 1 further comprising the step of separating and sequestering the carbon dioxide produced during the second step.
16. The process of claim 2 wherein at least a portion of the reduced oxygen carrier together with at least a portion of the fly ash are removed from the furnace.
17. The process of claim 16 wherein the amount of reduced oxygen carrier is fed into the furnace in an amount that is substantially the same as the amount of reduced oxygen carrier being removed from the furnace.
18. The process of claim 2 wherein at least a portion of the reduced oxygen carrier together with at least a portion of the fly ash are removed from the furnace and subsequently utilized as a ferroalloy addition in a process to produce an alloy material containing iron and slag.
19. The process of claim 5 further comprising the step of separating the carbon monoxide produced during the second step.
20. The process of claim 1 or claim 2 wherein the reduced oxygen carrier is a metal or a metal suboxide.
21. The process of claim 1 wherein the reduced oxygen carrier is a metal selected from the group consisting of rhenium, platinum, rhodium, palladium, copper, barium, manganese, molybdenum, vanadium, bismuth, lead, mercury, sodium, potassium, rubidium, and cesium.
22. The process of claim 2 wherein the oxygen carrier is substantially free-flowing.
23. The process of claim 1 wherein the fuel is selected from carbon, coal, hydrogen, hydrocarbon, biofuel, methane, natural gas, petroleum, crude oil, tar sands, oil shale, biomass, algae, fuel-rich waste gases from fuel cells, other fossil fuel or synthetic fuel.
24. The process of claim 2 wherein the ash-containing fuel is coal.
25. The process of claim 1 wherein the fuel is a carbon, a hydrocarbon, or hydrogen in the form of a solid, a liquid or a gas.
26. The process of claim 1 wherein the oxygen carrier is in the form of a powder.
27. The process of claim 26 wherein the oxygen carrier powder has a particle size of from 100 nanometers to 1 mm as determined by laser light scattering.
28. The process of claim 1 wherein the oxygen carrier is in the form of a powder having a particle size of from 20 microns to 250 microns as determined by laser light scattering.
29. The process of claim 1 wherein the fuel is a coal in the form of a powder.
30. The process of claim 29 wherein the coal powder has a particle size of from 100 nanometers to 10 mm as determined by laser light scattering.
31. The process of claim 1 wherein the fuel is a coal in the form of a powder having a particle size of from 20 microns to 250 microns as determined by laser light scattering.
32. The process of claim 1 wherein the fuel is coal having a particle size that is substantially similar to the particle size of the oxygen carrier.
33. The process of claim 1 wherein said oxidized oxygen carrier is at least partially vaporized during said second step of the process.
34. The process of claim 4 wherein the difference between said first reactor temperature and said first flash temperature in the first reactor is at least 300° C.
35. The process of claim 4 wherein the difference between said second reactor temperature and said second flash temperature in the second reactor is at least 300° C.
36. The process of claim 4 wherein the difference between said first reactor temperature and said first flash temperature in the first reactor is at least 800° C.
37. The process of claim 4 wherein the difference between said second reactor temperature and said second flash temperature in the second reactor is at least 800° C.
38. The process of claim 4 wherein the reduced oxygen carrier and the oxygen are fed into the first reactor at a rate sufficient to substantially off-set the heat loss of the first reactor and create a stable self-sustaining reaction zone within the first reactor.
39. The process of claim 4 wherein the oxidized oxygen carrier and the fuel are fed into the second reactor at a rate sufficient to substantially off-set the heat loss from the second reactor and create a stable self-sustaining reaction zone within the second reactor.
40. The process of claim 2 wherein the temperature within the first reactor is above the solid/liquid phase transition temperature of the reduced oxygen carrier.
41. The process of claim 2 wherein the temperature within the first reactor is above the solid/gas phase transition temperature of the reduced oxygen carrier.

42. The process of claim 2 wherein the temperature within the first reactor is above the liquid/gas phase transition temperature of the reduced oxygen carrier.

43. The process of claim 2 wherein the temperature within the second reactor is above the solid/liquid phase transition temperature of the oxidized oxygen carrier.

44. The process of claim 2 wherein the temperature within the second reactor is above the solid/gas phase transition temperature of the oxidized oxygen carrier.

45. The process of claim 2 wherein the temperature within the second reactor is above the liquid/gas phase transition temperature of the oxidized oxygen carrier.

46. The process of claim 3 wherein the residence time of the oxygen and the reduced oxygen carrier in the first reactor is from 0.01 to 1.0 minute.

47. The process of claim 3 wherein the residence time of the oxygen and the reduced oxygen carrier in the first reactor is from 0.01 to 10 seconds.

48. The process of claim 3 wherein the process is performed in a flash furnace and the residence time of the fuel and the oxidized oxygen carrier in the second reactor is from 0.01 seconds to 1.0 minute.

49. The process of claim 3 wherein the process is performed in a flash furnace and the residence time of the fuel and the oxidized oxygen carrier in the second reactor is from 0.01 seconds to 10 seconds.

50. The process of claim 4 wherein the reduced oxygen carrier flows concurrently in the same direction with the flow of the oxygen in the first reactor.

51. The process of claim 4 wherein the oxidized oxygen carrier flows concurrently in the same direction with the flow of the fuel in the second reactor.

52. The process of claim 5 wherein the fuel and the oxidized oxygen carrier are fed into the second reactor in substantially stoichiometric amounts.

53. The process of claim 5 wherein the fuel and the oxidized oxygen carrier are fed into the second reactor in less than stoichiometric amounts in order to produce carbon monoxide.

54. A process for generating useful work comprising the process of claim 1.

55. A process for generating useful work comprising the first step of the process of claim 1.

56. A process for generating useful work comprising the second step of the process of claim 1.

57. The process of claim 1 further comprising utilizing the energy produced during the exothermic process in a generator for generating electricity.

58. The process of claim 1 further comprising converting the energy produced during the exothermic process into steam that is used to rotate a turbine engine.

59. The process of claim 1 wherein the steps can be performed in either order.

60. The process of claim 4 further comprising (d) feeding carbon dioxide into said second reactor.

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