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Thermodynamic Laws of Impurities in the Titanium Sponge Inflow during its Production

Ivan Fedorovich CHERVONYJ (UA) rot44@ya.ru
Dmytro Olexandrovich LISTOPAD (UA) TitanTitanovich@ya.ru

ABSTRACT

There are the key rules discussed of spongy titanium production process by Magnesium thermal reduction of Titanium tetrachloride. Thermodynamic analysis carried out of the possible effects of interaction of alloying elements (Molybdenum, Tungsten, Niobium, Tantalum, Zirconium), as well as interaction reactions of the main components (Iron, Chromium, Manganese, Nickel) with Titanium chlorides and with oxygen, as for Magnesium thermal method of Titanium obtaining.

KEY WORDS

Titanium sponge, Titanium chlorides, reactor, alloying elements, impurities.

INTRODUCTION

Technology of titanium sponge reduction is the reduction of titanium tetrachloride by molten magnesium in a steel sealed reactor by the method of Kroll [3]. Apparatus for titanium sponge reduction by magnesium thermal method consists of the electric shaft furnace, the reduction device, communications to $TiCl_4$ supply, argon, water, process control and regulation devices. On the inner surface of the furnace lining there are nichrome heaters suspended, which are distributed by heating zones (Fig. 1).

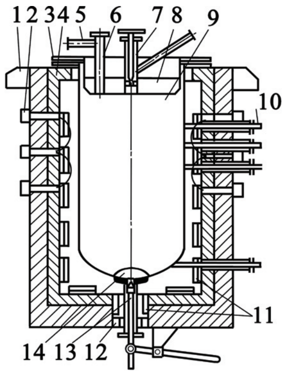


Fig. 1: *Scheme of reduction apparatus with the lower drain, placed in the oven [3]. 1 – the furnace mount, 2 – collector of air feed and withdrawal, 3 – water-cooled flange connection, 4 – furnace lining, 5 – degassing and argon supply bean; 6 – unit of magnesium casting, 7 – feeding unit of* $TiCl_4$*; 8 – reactor cover, 9 – retort, 10 – contact thermometers (thermoprobes), 11 – heaters, 12 – sand shutter; 13 – rod of drain device, 14 – the false bottom.*

In the furnace there is reactor coolant system located for cold and hot air removal. The main element of the device reduction is the reactor (Fig. 1), that is a cylinder of stainless steel 12X18H10T of thickness of 15 – 25 mm with a spherical bottom and water-cooled flange. The lid of apparatus serves its hermetic sealing. There are units placed to feed the apparatus with parent substances and inert gas, as well as a device to drain magnesium chloride, accumulated in the reactor. Purified titanium tetrachloride is injected in pressurized reactor (Fig. 2) filled with argon, which previously was filled with purified magnesium. Reduction of titanium tetrachloride with magnesium is a complex heterogeneous process, it is accompanied by a significant heat release, as well as continuous change in the surface area of forming reaction mixture. Technological proprocess and the nature of the formation of reaction mass is regulated by changing the rate of introduction of titanium tetrachloride, temperature of the reduction process and treatment of magnesium chloride discharge [5] with the purpose of obtaining a regulated product composition. This method is established due to successful combination of properties in the system $Ti - TiCl_4 - Mg - MgCl_2$. Magnesium has a significantly higher chemical affinity for chlorine than titanium. Titanium, magnesium and magnesium chloride are almost mutually insoluble. Ratio of melting and boiling temperatures of magnesium and magnesium chloride is favorable for the reduction process in a wide range of temperatures: from 720 to 1410 °C [3]. However, the maximum temperature is limited by steel gear resistance, because above 1000 °C contact of titanium with the material of the reactor could lead to the formation of eutectics alloys and burning out wall of the reactor, as well as the transition of iron and nickel in the sponge layers adjacent to wall to a depth of about 20 – 40 mm. This process lead to sponge contamination [1, 8].

As intermediate products of $TiCl_4$ reduction there are lower titanium chlorides formed ($TiCl_3$ and $TiCl_2$) which act onto reactor material with transition of steel components to chloride compositions. During reduction process there is a need to maintain reactor wall temperature within 820 – 850 °C. For this purpose there are nichrome heaters and air coolers placed in a furnace where reactor is located. With in-turn switching on of heaters and coolers the temperature is regulated. After the process the reactor is cooled with air and water, which causes the formation of scale - the main reason influencing the decrease in wall thickness of expensive reactor, causing it unfitness.

The resultant titanium looks spongy mass - "reaction mass" that represents a block of titanium sponge, whose pores are filled with magnesium chloride and unutilized magnesium. For cleaning of titanium there is process of vacuum separation of the reaction mixture used, carried out in a vacuum in the apparatus at temperatures up to 1020 °C. The rate of heating of reaction mass unit and the condensation of sublimates [3] in the first period are the main factors determining the speed of process of vacuum separation. Components sublimated and condensed in the back retort of the reaction mass (condensate) are directed in circulation for use in the next reduction process. Titanium in the form of spongy block is pressed out or is distracted from the retort. The structure of titanium sponge, its physical characteristics (specific surface area, porosity) reflect total influence of various parameters, both during the reduction process and vacuum separation (Fig. 3). Quality of spongy block varies in different parts of the block that is why there are differential cutting and sorting used, for which impurities-rich peripheral parts (crust, the lower classes) are separated from the block. Then titanium sponge is crushed and sorted. The resulting material is a commercial product.

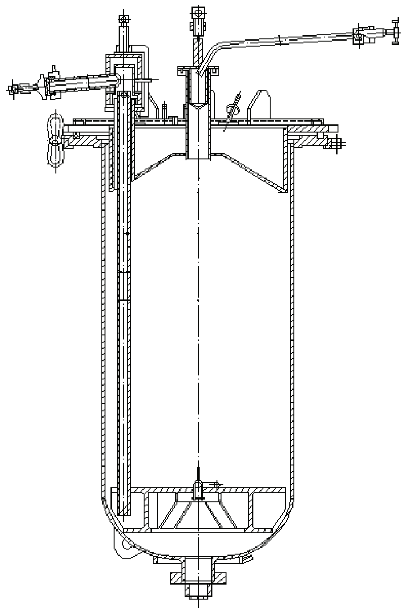


Fig. 2: *Reactor scheme with upped discharge for* $TiCl_4$ *reduction.*

The quality of titanium sponge is determined by the content of impurities in it. The lower content of impurities, the higher the quality of titanium sponge. Sources of impurities are:

- Raw materials (Mg and $TiCl_4$, argon).
- Equipment (material of the reactor).
- The environment (air leaks in vacuum separation).

Receipt of impurities from raw materials and the environment will not be considered in this work. The objective is: thermodynamic analysis of the interaction of metals (Fe, Cr, Ni, Mn) with chlorides of titanium and oxygen, and finding possible sources of impurities in the titanium sponge material from the retort.

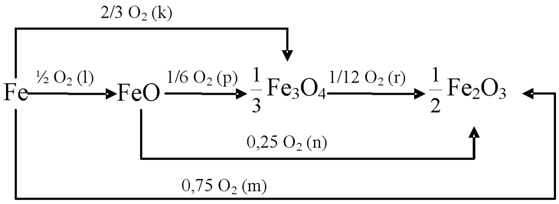
Fig. 3: *Appearance of titanium sponge [7, 4].*

RESEARCH METHODOLOGY

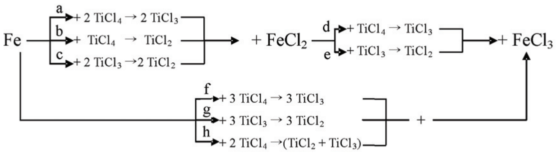
For the theoretical study of the behavior of the main components of steel (Fe, Cr, Ni, Mn) under the influence of oxygen and titanium chlorides there were calculated thermodynamic probability processes of interaction of alloying elements with chlorides of titanium and oxygen. Graphical representation of the possible ways of proceeding of processes is performed on schemes. On these schemes between the basic metals and products of oxidation there are arrows shown with influencing reagents and reaction products formed. Moreover, reagents and reaction products are given with coefficients factored into the calculations. If there are several alleged ways of transfer among several agents, then the scheme of these paths are shown above each other and should be understood as an individual reactions. Schemes show the possibility of formation of lower oxides and chlorides of the metal alloy and their interaction with the lower chlorides of titanium. According to the rules adopted in metallurgical thermodynamics, calculations carried out at 1 mol-atom of metal, and if the reaction formed a substance with a multiple number of atoms (Fe_3O_4, Cr_2O_3, etc.) - then the coefficients were divided by this divisible number to obtain the equation with fractional coefficients [2]. Since number of the assumed reactions with some of the elements is large, then for readability there were several plots constructed for each element of Gibbs energy change of temperature. Each graph shows no more than nine reactions. Also for the readability of graphs over the arrows in the numbering scheme of reactions carried out in Russian letters in parentheses for chlorides and Latin - for oxides, but below the graphs, each line denotes the corresponding reaction and character.

Let us consider the behavior of the main components of the reactor material.

Iron. Formations of three iron oxides for possible reactions with oxygen are presented in the scheme:



Possible ways of interaction of iron and its compounds with titanium chlorides are presented on scheme:



At interaction of iron with titanium chlorides at reactions (”a”, ”b”, ”c”) there are lower titanium chlorides and iron chloride (II) $FeCl_2$ formed. After than iron chloride (II), in the same media repeatedly interacts with titanium chlorides, at reactions ”d” and ”c”, with formation of iron chloride (III) $FeCl_3$. Straight iron oxidation into iron oxide (III) is possible at reactions ”f”, ”g” and ”h”.

Among graphs shown at Fig. 4 it can be assumed that iron interaction with titanium chlorides can go only in several ways of above-mentioned ones. Reaction ”a” goes at temperatures up to 800 K and higher than 1200 K. Reactions ”b” and ”f” can proceed at temperatures up to 600 K and 500 K respectively. Higher than these temperatures, reactions cannot proceed for the thermodynamics reasons. There is shown that iron oxides formation as a result of interaction with oxygen is possible for the thermodynamics reasons at all the discussed temperature range.

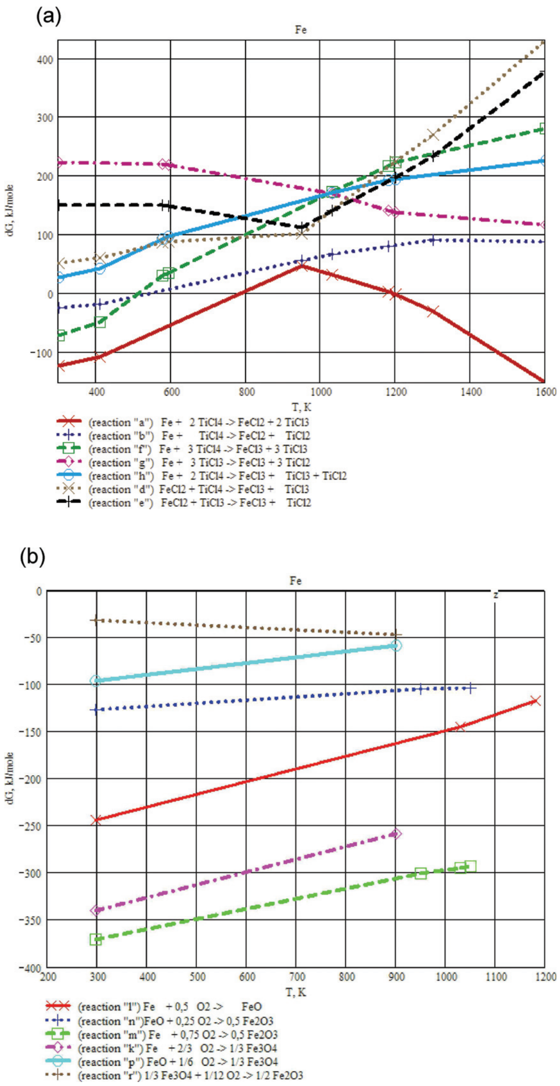
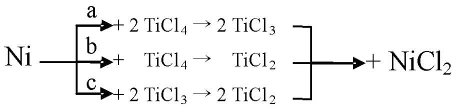


Fig. 4: *Temperature dependences ΔG_T of possible ways of metallic iron and its compounds oxidation at interaction with titanium chlorides (a) and oxygen (b). *Dependence graph ΔG_T of reaction ”c” was not built because obtained values (300 … 520 kJ/mol) witness that at no considered temperature process is thermodynamically possible.*

Nickel forms bivalent compounds. Possible reactions of nickel dichloride and nickel oxide formation are shown at scheme:



$$Ni + \frac{1}{2} O_2 \rightarrow NiO$$

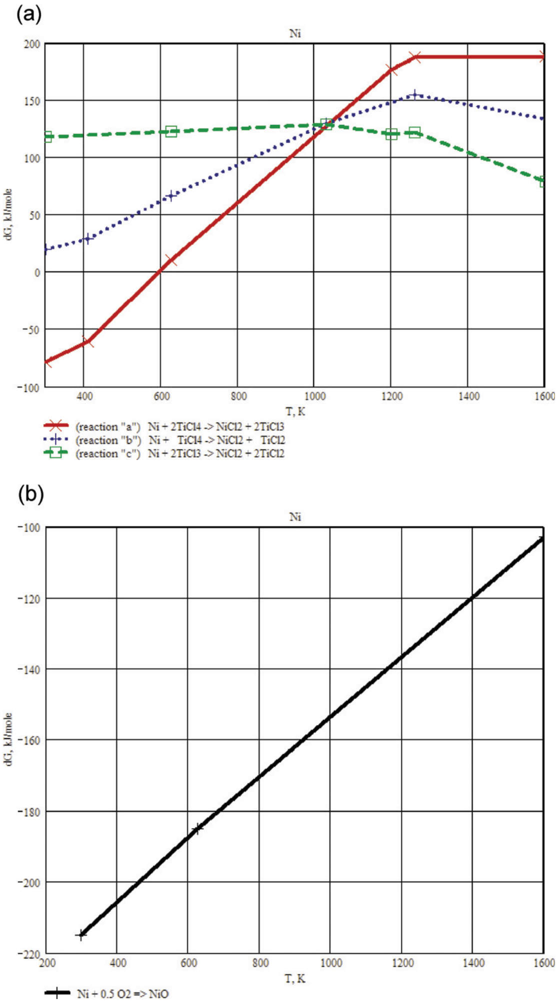
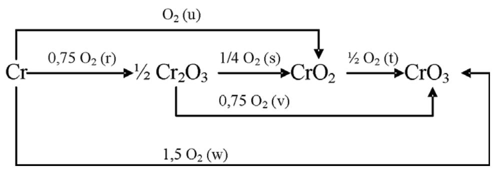


Fig. 5: *Temperature dependences ΔG_T of possible ways of metallic nickel and its compounds oxidation at interaction with titanium chlorides (a) and oxygen (b).*

Graphs (Fig. 5) allow us to say that the formation of nickel oxide is thermodynamically possible at all the considered temperature range. However, nickel as well as chromium, form a dense oxide layer, which protects the metal from further oxidation. The interaction of chlorides of titanium and nickel is thermodynamically possible at temperatures up to 600 K by the reaction "a". Course of other reactions in the forward direction is thermodynamically not possible at all considered temperatures. Thus nickel can not act in a titanium sponge through the stage of formation of chlorides. The bulk of the nickel gets into titanium sponge material from the reactor through the interaction with the molten magnesium and the formation of intermetallic compounds of magnesium Mg_2Ni and $MgNi_2$ [6], as well as by thermal diffusion.

Chrome. There are three stable chromium oxide (Cr_2O_3, CrO_2 and CrO_3), the possible reaction of these substances under the influence of atmospheric oxygen on the wall of the reactor are presented in the scheme:



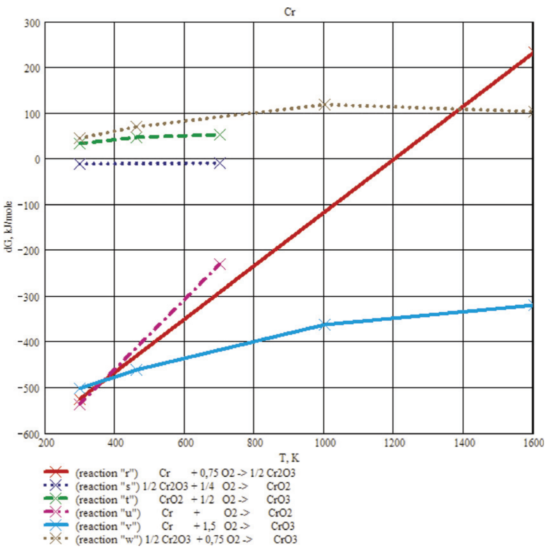
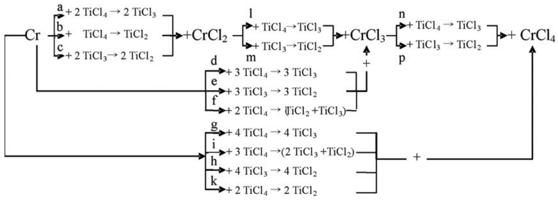


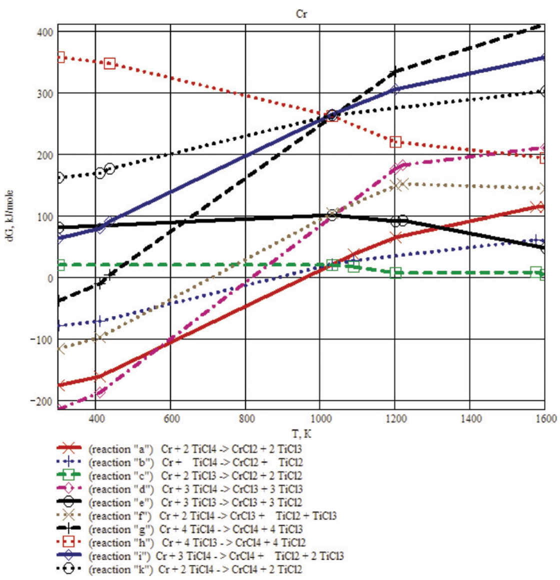
Fig. 6: *Temperature dependences ΔG_T of possible ways of metallic chrome and its chloride oxidation under action of oxygen.*

Graphs (Fig. 6) show that the formation of all three oxides of chromium is thermodynamically possible, but in practice, the oxidation of chromium may be hindered due to dense oxide film of Cr_2O_3 on the metal surface, which prevents the formation of oxides. Reactions of oxidation of lower oxides to higher degrees of oxidation is thermodynamically unfavorable process.

Reaction of chromium chloride formation $CrCl_2$, $CrCl_3$, $CrCl_4$ under the influence of titanium chloride, is depicted in the scheme:



From temperature dependences (Fig. 7) is seen that chrome and its chlorides can interact with titanium chlorides at low temperatures (about 1000 K), at higher temperatures such an interaction is thermodynamically possible. That is why chrome impurities intrusion into sponge titanium does not go nor through chloride formation stage neither by thermal diffusion.



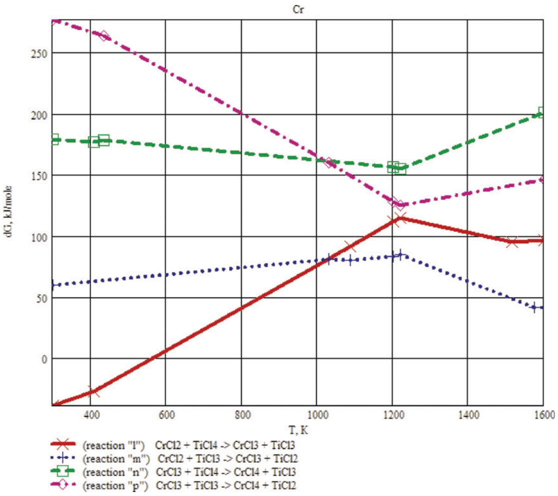
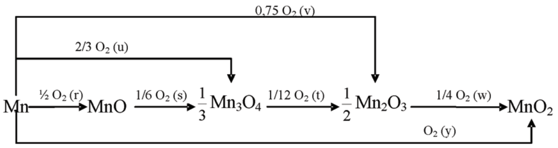


Fig. 7: *Temperature dependences* ΔG_T *of possible ways of metallic chrome and its chloride oxidation at interaction with titanium chlorides.*

Manganese. Manganese and its oxides interaction with oxygen is described by the scheme:



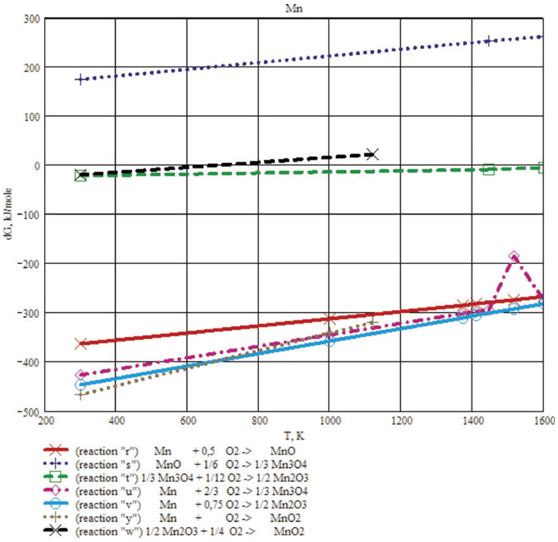
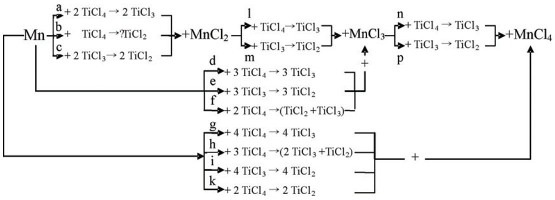


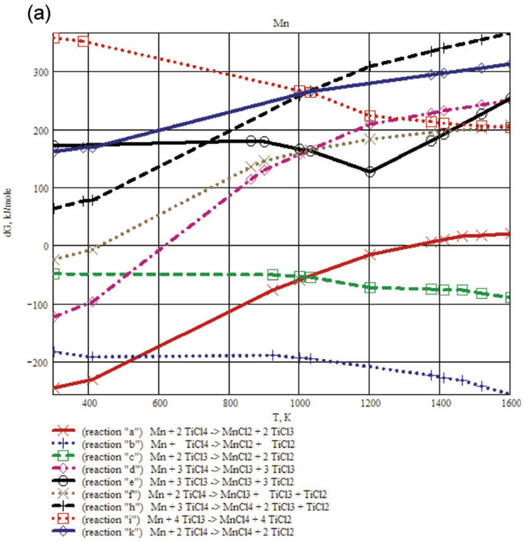
Fig. 8: *Temperature dependences* ΔG_T *of possible ways of metallic manganese and its oxide oxidation under action of oxygen.*

The curves in Fig. 8 show that the formation of all three of manganese oxides is thermodynamically favorable on the whole considered range of temperatures, but further oxidation of manganese oxides to higher oxidation states is difficult. For reactions of "t" and "w" values of Gibbs energy is close to zero, hence there is chemical equilibrium possible among Mn_2O_3, Mn_3O_4 and MnO_2, and the oxidation of MnO to Mn_2O_3 by oxygen in manganese-thermal production of titanium is thermodynamically impossible in the whole considered temperature range.

Possible ways of formation of chlorides of manganese under the influence of titanium chlorides are presented at scheme:



Reactions of manganese influence on $TiCl_4$ and $TiCl_3$ with the formation of $MnCl_2$ ("a", "b" and "c"), is the most thermodynamically probable processes (Fig. 9). The further oxidation of MnCl2 is thermodynamically impossible. However, the flow of impurities in the magnesium block of spongy titanium does not occur in the low (less than 1 %) content of manganese in steel used for the manufacture of reactor.



(b)

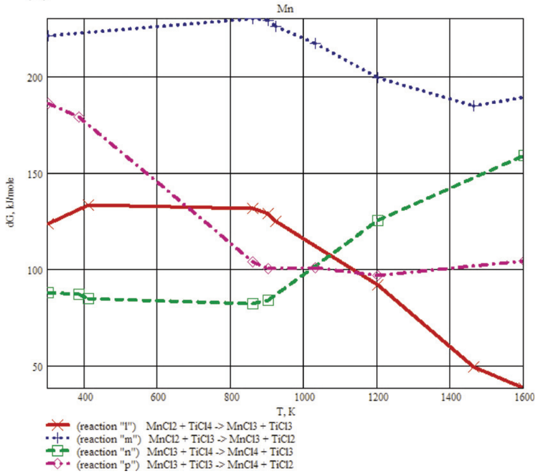


Fig. 9: *Temperature dependences ΔG_T of possible ways of metallic manganese and its chlorides oxidation at interaction with titanium chlorides *Dependence graph ΔG_T of reaction "g" was not built because obtained values (720 … 1520 kJ/mole) witness that at no considered temperature process is thermodynamically possible.*

CONCLUSIONS

On a basis of thermodynamic calculations there is determined that:

- Iron is converted into titanium sponge as a result of interaction with titanium chlorides by thermal diffusion. At the same time the formation of iron oxides may go at any of the proposed reactions in the whole considered temperature range which means that during the operation of the reactor intensive formation of iron slag (a mixture of iron oxides) takes place, as well as thinning of the reactor's material, which leads to premature failure of expensive equipment.

- Nickel does not react with titanium chlorides in manganese-thermal production of titanium sponge (at T=1100–1150 K), so the bulk of nickel enters the sponge titanium through as an impurity through stage of formation of intermetallic compounds Mg_2Ni and $MgNi_2$, as well as by thermal diffusion way.

- Chromium does not react with chlorides of titanium at temperatures above 1000 K, and does not turn into a titanium sponge by thermal diffusion, so in the titanium sponge there is no appreciable amounts of chromium, and there is no need to control its content. Formation of chromium oxides is thermodynamically possible, but in practice they are not formed in significant quantities, because the oxide film on the surface of chromium prevents this process.

- Manganese under the influence of titanium chlorides becomes $MnCl_2$, and under the influence of oxygen is converted into oxides - these processes are thermodynamically possible in the whole considered temperature range. However, due to the low concentration of manganese in steel 12X18H10T (1 %) transition of manganese does not affect the quality of the titanium sponge.

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