D. V. Bachurskiy; I. F. Chervoniy, Dr. Sc. (Eng.), Prof.

BEHAVIOUR OF TITANIUM ADMIXTURES IN ELECTROLYTES OF MAGNESIUM ELECTROLYZERS

The paper contains the results of thermodynamic calculations and modeling of the interaction of the compounds of titanium, humidity, oxygen and magnesium oxide in the melt of potassium electrolyte, used in electrolytic production of magnesium. The results obtained show the possibility of coprecipitation of titanium admixtures and magnesium oxide into the slime.

Key words: *thermodynamics, thermodynamic modeling, electrolysis of magnesium, lower titanium chloride, humidity.*

Introduction

Magnesium for thermo reduction of titanium at titanium-magnesium plants of Ukraine, Russia and Kazakhstan is produced using electrolytic method. The technology of electrolytic production of magnesium is based on electrolytic decomposition of magnesium chloride, on the background of melted mixture of chlorides of alkali and alkali-earth metals. The source of magnesium chloride may be carnality or reversed magnesium chloride of titanium production. Nowadays due to the lack of carnalite as the raw material, reversed magnesium chloride is used. This kind of raw material contains admixtures, which may have negative impact on the process of electrolysis and considerably worsen technical and economic indices of magnesium production. One of the most harmful admixtures is titanium. This admixture in magnesium chloride is in the form of highly dispersed metal and lower titanium chlorides. Neutralization of the negative impact of titanium compounds on electrolysis indices is actual and important problem.

Analysis of research and publications

Minimal admissible content of titanium in electrolyte is 0.005 % mas. [1, 2]. Excess of this value over 0.008 % mas. in raw material violates the normal course of electrolysis, that results in cathode passivation, liberation of magnesium in the form of fine beads which do not melt and decrease of magnesium output by 5 ÷ 10 %. [3]. Titanium in reversed magnesium chloride is mainly in the form of lower chlorides $TiCl_2$, $TiCl_3$. These compounds are soluble in electrolytes, used in magnesium production. At contact with air or other sources of water and oxygen these compounds are decomposed and transfer into insoluble oxide form [4]. This process favors the elimination of titanium compounds from electrolyte into slime.

Problem set-up

In order to understand the mechanism of titanium transition in the electrolyte of magnesium electrolyzer from soluble to insoluble form using program «TERRA» [5], thermodynamic modeling of balanced composition of the set system was performed. Thermodynamic calculation of possible chemical reactions of titanium compounds $TiCl_2$, $TiCl_3$ with water and oxygen were carried out.

Discussion of the research results and publications

Calculations were carried out at 1000 g of potassium electrolyte. Temperature values corresponded to operating temperature of magnesium electrolyzers. The content of titanium and amount of water to be added were chosen for the convenience of further experimental research.

The following conditions were selected for the simulation:

- composition of electrolyte - $MgCl_2$ 22 %, mass., relation in electrolyte KCl: NaCl = 3:1;
- content of Ti_{tot} = 0.1 % mass., quantity of $TiCl_2$ = 1.88 g, $TiCl_3$ = 0.86 g;
- temperature 963, 1023 K;
- pressure 0.101 MPa;
- amount of water to be added to the melt 0.2; 0.5; 1.0; 1.5; 2.0; 6.0 g.

Water may be supplied to the melt in the compound of humidified common salt – NaCl or with the air.

Fig. 1, 2 contains diagrams of the relations of system components products interaction.

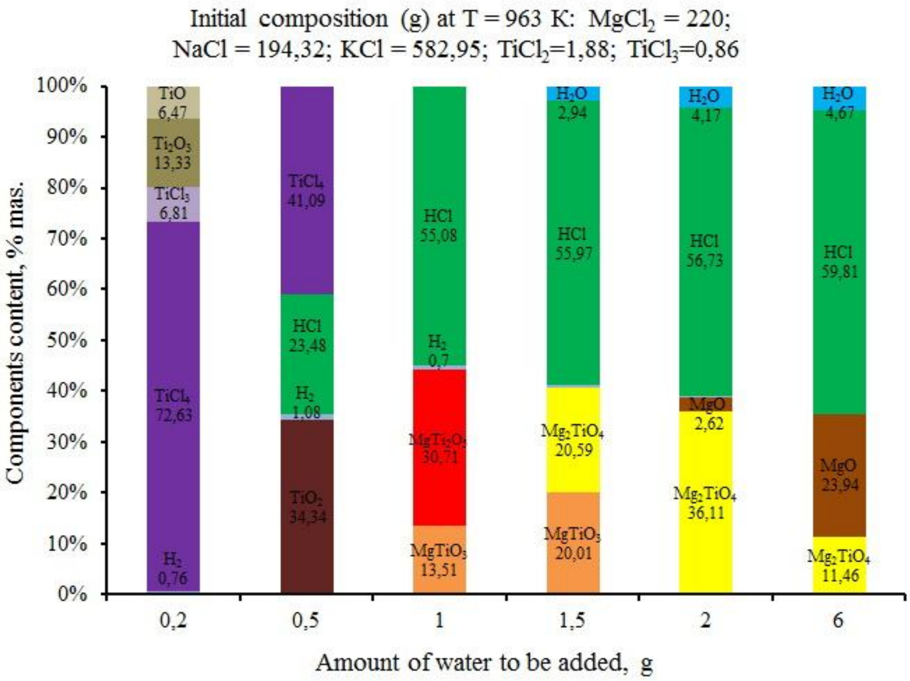

Fig. 1. Relation of systems components products interaction at the temperature 963 K

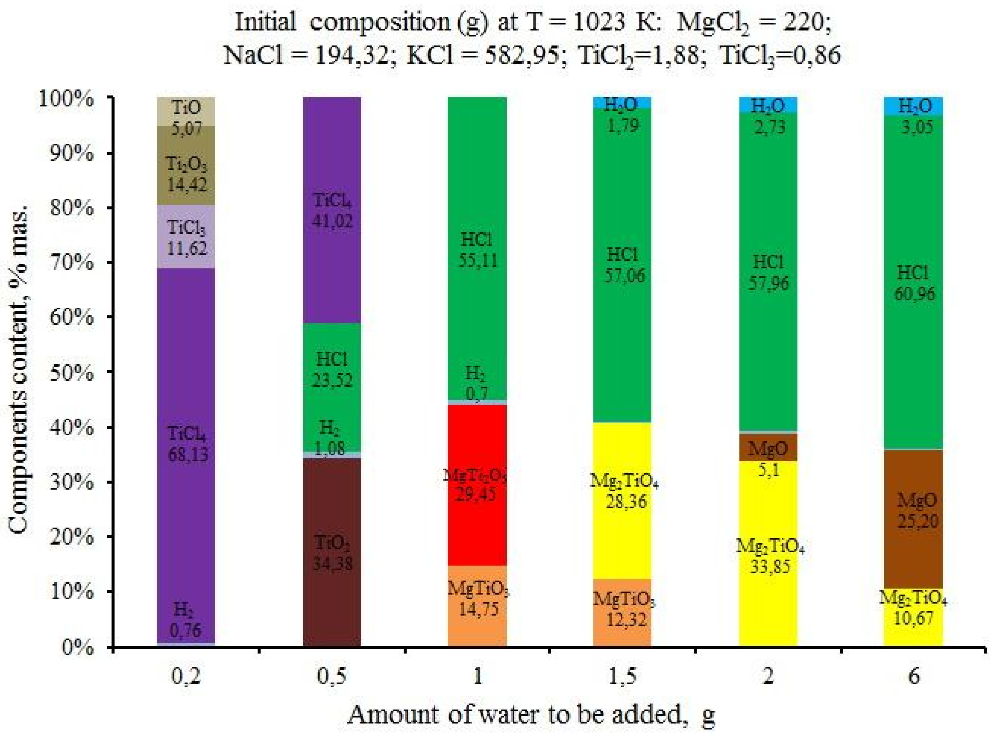

Fig. 2. Relation of systems components products initeraction at the temperature 1023 K

It is seen from the diagrams that in case of equilibrium common compounds of magnesia and titanium dioxide, namely magnesium titanates are formed: $MgTi_2O_5$, $MgTiO_3$, Mg_2TiO_4. At smaller amount of water first of all titanium oxides TiO, Ti_2O_3 are formed. Also $TiCl_4$ is formed, this compound due to weak interaction with metal chlorides of electrolyte and high spring of vapors, evaporates from the melt It should be noted, that with temperature growth, if other conditions are equal, the system tends to creation of greater amount of MgO.

Calculation of system balanced composition dependence on the amount of water, arriving to the melt, is shown in Fig. 3. With the increase of water content, more complex compounds of titanium and magnesium are formed. However, it is seen from dependences, shown in Fig. 1, 2 and 3, that in creased humidification of the salt or air leads to additional formation of magnesia and results in the losses of magnesium.

While thermodynamic modeling of the process possible formation of $NaTiCl_3$, Na_2TiCl_4, $NaTiCl_4$, Na_2TiCl_5, K_2MgCl_4 salts was not taken into account as the energy of interaction of lower titanium chlorides with melt components does not influence the possibility of other reactions proceeding in electrolyte [1, 6]. Thermodynamic calculations of possible chemical reactions of titanium compounds with water and oxygen were performed, it enabled to substantiate the scheme of magnesium titanates formation.

Data for thermodynamic calculations were taken from [7]. Calculations were performed by the formula:

$$\Delta G_T^0 = \Delta H_T^0 - T \cdot \Delta S_T^0 , \qquad (1)$$

where – ΔG_T^0 – change of Gibbs thermodynamic potential, KJ/mol, – ΔH_T^0 – change of thermal effect, KJ/mol, – ΔS_T^0 – entropy change, J/(mol·K), – T – temperature, K.

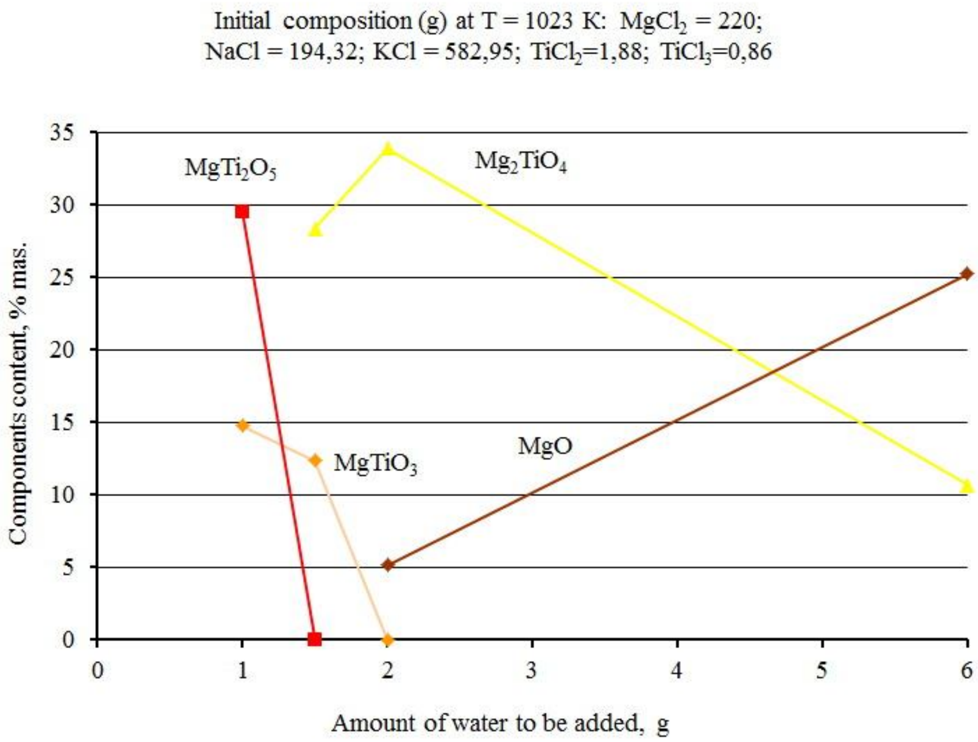

Fig. 3. Change of magnesium titanates relation in electrolyte depending on the amount of water, arriving to electrolyte

All the reactions were divided into levels, according to the stages of interaction. Possible reactions which may occur as a result of electrolyte contact with oxygen and moisture of the air, and water in humidified common salt may be referred to the reactions of the first level.

Table 1

Calculation values of Gibbs thermodynamic potential of reactions at the temperature 963 and 1023 К (reactions of the first level)

№ of the reaction	Chemical reaction	$\Delta G_{(963)react.}$, KJ/mol	$\Delta G_{(1023)react.}$, KJ/mol
1	$2MgCl_2+O_2=2MgO+2Cl_2$	-12,97	-21
2	$TiCl_2+O_2=TiO_2+Cl_2$	-275,17	-272,74
3	$2TiCl_2+O_2=TiO_2+TiCl_4$	-376,42	-371,36
4	$2TiCl_3+2O_2=2TiO_2+3Cl_2$	-380,58	-382,84
5	$4TiCl_3+O_2=TiO_2+3TiCl_4$	-239,4	-243,35
6	$MgCl_2+H_2O=MgO+2HCl$	-129,97	-148,29
7	$TiCl_2+2H_2O=TiO_2+2HCl+H_2$	-660,239	-685,62
8	$2TiCl_3+4H_2O=2TiO_2+6HCl+H_2$	-1012,62	-1071,3
9	$2TiCl_3+H_2O=TiO+2HCl+TiCl_4$	-111,83	-133,24
10	$2TiCl_3+3H_2O=Ti_2O_3+6HCl$	-587,37	-637,96

The given results of calculations show thermodynamic probability of reactions 1…10 flow, taking into account values of $\Delta G_{(963)}$, $\Delta G_{(1023)}$ in the following sequence: 8, 7, 10, 4, 3, 2, 5, 6, 9, 1. From the reactions, given above, it is seen that chemical components of the melt will react rather with water than with oxygen. As the content of …lower… titanium chlorides in electrolyte is several orders lower than magnesium chloride, reactions 6 and 1 (Table 1) will flow in the melt first of all. Further, taking into account the least ΔG_{react}, reactions, accompanied by formation of titanium oxide (II), hydrogen chloride and hydrogen.

As during the reactions of the first level lower titanium chlorides and magnesia may be in the melt, considering sodium chlorides and potassium chlorides to be inert background, we will evaluate the probability of interaction of lower titanium chlorides with titanium oxide, that was formed .

Table 2

Calculation values of Gibbs thermodynamic positional of reactions at the temperature 963 and 1023 К (reactions of the second level)

№ of the reaction	Chemical reaction	$\Delta G_{(963)react.}$, KJ/mol	$\Delta G_{(1023)react.}$, KJ/mol
11	$TiCl_2+MgO=TiO+MgCl_2$	-50,37	-48,96
12	$2TiCl_3+3MgO=Ti_2O_3+3MgCl_2$	-197,46	-193,1

Reaction 12 will take place first, the data of the reactions will proceed better at decreased temperature. Formed titanium oxides (II) and (III) can be further oxidized [8] according to the reactions of the third level:

Table 3

Calculation values of Gibbs thermodynamic potential of reactions at the temperature 963 and 1023 К (reactions of the third level)

№ of the reaction	Chemical reaction	$\Delta G_{(963)react.}$, KJ/mol	$\Delta G_{(1023)react.}$, KJ/mol
13	$2TiO+O_2=2TiO_2$	-436,64	-426,56
14	$2Ti_2O_3+O_2=4TiO_2$	-327,34	-316,48
15	$2TiO+H_2O=Ti_2O_3+H_2$	-534,55	-543,42
16	$Ti_2O_3+H_2O=2TiO_2+H_2$	-425,25	-433,34

Reactions of the interaction of titanium oxide (IV) and magnesium titanates with magnesium oxides are referred to the reactions of the fourth level.

Table 4

Calculation values of Gibbs thermodynamic potential of reactions at the temperature 963 and 1023 К (reactions of the fourth level)

№ of the reaction	Chemical reaction	ΔG(963)react., KJ/mol	ΔG(1023)react., KJ/mol
17	2TiO2+MgO=MgTi2O5	-16,88	-16,77
18	TiO2+MgO=MgTiO3	-20,38	-19,76
19	TiO2+2MgO=Mg2TiO4	-16,74	-16,84
20	MgTi2O5+2MgO=MgTiO3+Mg2TiO4	-20,23	-19,83
21	MgTiO3+MgO=Mg2TiO4	3,64	2,92

Negative ΔG_{react} show the possibility of reactions 13...20 (Table 3, 4). Interaction by the reaction 21 at the given conditions does not take place, for its realization higher temperature is needed.

On the basis of thermodynamic analysis, carried out, the conclusion is made, regarding the possibility of chemical reactions flow , considered in Tables 1 – 4. At the first stage (reactions of the first level) the interaction of electrolyte with water and oxygen, accompanied by the formation of titanium oxides (II), (III), (IV), and magnesium oxides takes place. After formation of magnesia in electrolyte it interacts with remains of $TiCl_2$ and $TiCl_3$, which did not react at the first stage. At the second stage (reactions of the second level) lower titanium oxides(11) (111) are formed additionally. Lower titanium oxides, formed at the second stage of interaction, in their turn are oxidized to titanium oxide (IV) and the above-mentioned chemical reactions form third (reactions of the third level) stage of interaction of electrolyte with water and oxygen. Chemical reactions of titanates magnesium formation, shown in Table 4 are referred to the fourth (reactions of the fourth level), final stage of interaction.

Conclusions

1. Thermodynamic calculations and modeling of balanced composition of electrolyte showed the principle possibility of the considered reactions flow in magnesium electrolyzer if admixtures of titanium are present.

2. More possible are processes of interaction of the compounds of titanium and magnesia that can contribute to faster elimination of these admixtures into the slime.

REFERENCES

1. Бараннік І. А. Дослідження впливу домішок титану на процес електролізу хлористого магнію і якість металу: дис. … канд. техн. наук : 05.16.02 / Бараннік Іван Андрійович. – Дніпр., 1969. – 210 с.

2. Промислові дослідження впливу домішок титану на електроліз хлориду магнію / І. А. Бараннік, З. В. Ястребова, А. П. Єгоров [та ін.] // Цвет. мет. – 1971. – № 8. – С. 40 – 42.

3. Ветюков М. М. Електрометалургія алюмінію и магнію / Ветюков М. М., Циплаков А. М., Школьніков С. Н. – М. : – Металургія, 1987. – 320 с.

4. Бараннік І. А. Поведінка домішок титану при електролізі хлориду магнію / І. А. Бараннік, Л. Н. Антіпін // Збірник праць всесоюзної міжвузівської конференції з теорії процесів кольорової металургії. – Алма-Ата, 1971. – С. 293 – 300.

5. Трусов Б. Г. Програмний комплекс TERRA для розрахунків плазмохімічних процесів // Мат-лы III Міжнар. симп. по теоретичній і прикладній плазмохімії. – Плес, 2002. – С. 217 – 218.

6. Щьоголєв В. І. Електролітичне отримання магнію / В. І. Щьоголєв, О. А. Лєбєдєв. – М.: Руда і метали, 2002. – 368 с.

7. Термодинамічні властивості неорганічних речовин. : довідник / [Верятин У. Д., Маширєв В. П., Рябцев Н. Г. та ін.] ; під ред. А. П. Зефірова. – М.: – Атомвидат, 1965. – 452 с.

8. Лучинський Г. П. Хімія титану / Лучинський Г. П. – М.: – Хімія, 1971. – 472 с.

Bachurskiy Denys – Post Graduate, with the Department of Non-Ferrous Metallurgy, tel.: +380663952808; (061)289-81-64, E-mail: denis-bacho@yandex.ru.

Chervoniy Ivan **–** Dr. Sc. (Eng.)**,** Professor, Head of the Chair of Non-Ferrous Metallurgy.
Zaporizhia State Engineering Academy.