NACIONĀLAIS ATTĪSTĪBAS PLĀNS 2020

EIROPAS SAVIENĪBA
Eiropas Reģionālās attīstības fonds

IEGULDĪJUMS TAVĀ NĀKOTNĒ

Latvijas Universitātes
Fizikas Institūts

Elektrosārņu process labākai titāna nogulsnējumu morfoloģijai

Projekts Nr. 1.1.1.1./16/A/85
(Progresa ziņojums - 3)

2017
01.09. –07.11.

Projektā piedalās:

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3	Zablockis	Dmitrijs
4	Goldšteins	Linards
5	Majorovs	Mihails
6	Blumbergs	Ervīns
7	Kagaļņickovs	Vadims
8	Serga	Vera
9	Ivanovs	Sergejs
10	Krūmiņa	Aija
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Projekta uzdevums :

- Veikt rūpnieciskos pētījumus ar mērķi izstrādāt jaunu tehnoloģiju, kas balstīta uz Krola un elektrosārņu procesiem un tehnoloģijas prototipu Ti/TiAl sakausējumu iegūšanai.

Projekta rezultāti:

- Jābūt izveidotam jaunas Ti/TiAl sakausējumu iegūšanas tehnoloģijas prototipam;
- Jābūt apstiprinātai un aizstāvētai projekta izpildes gaitā izstrādātajai tehnoloģijai patenta formā, publicētiem 4 oriģināliem zinātniskiem rakstiem un 8 ziņojumiem starptautiskās konferencēs.

Satura rādītājs

Ievads.

Tā kā jaunās titāna un tā savienojumu iegūšānas metodes pamatā ir titāna tetrahlorīda metalotermiskā reducēsana izmantojot kausētu kušņu slāni, kurš darbojas kā viedā puscaurlaidīga mambrāna, ir jāizpēta kušņu slāņa spēju izfiltrēt cauri tam titānu, atdalīt reaktorā karsto zonu (1700 – 1750 C) no nosacīti aukstās (1200 – 1400^0 C), kā ari vienlaicīgi pievadīt titāna pārkausēšanai nepieciešamo papildus termisko enerģiju izmantojot elektrosārņu pārkausēšanas procesu, tāpēc projekta 3. Etapa (09.-10.2017.) izpildes procesā galvenā uzmanība bija pievēsta eksperimentālās iekārtas reaktora moduļa stenda izstrādei un kušņu īpašību analīzei.

Aktivitāte Nr. 1. Tehnoloģijas prototipa izstrāde, integrējot galvenās tehnoloģiskās komponentes

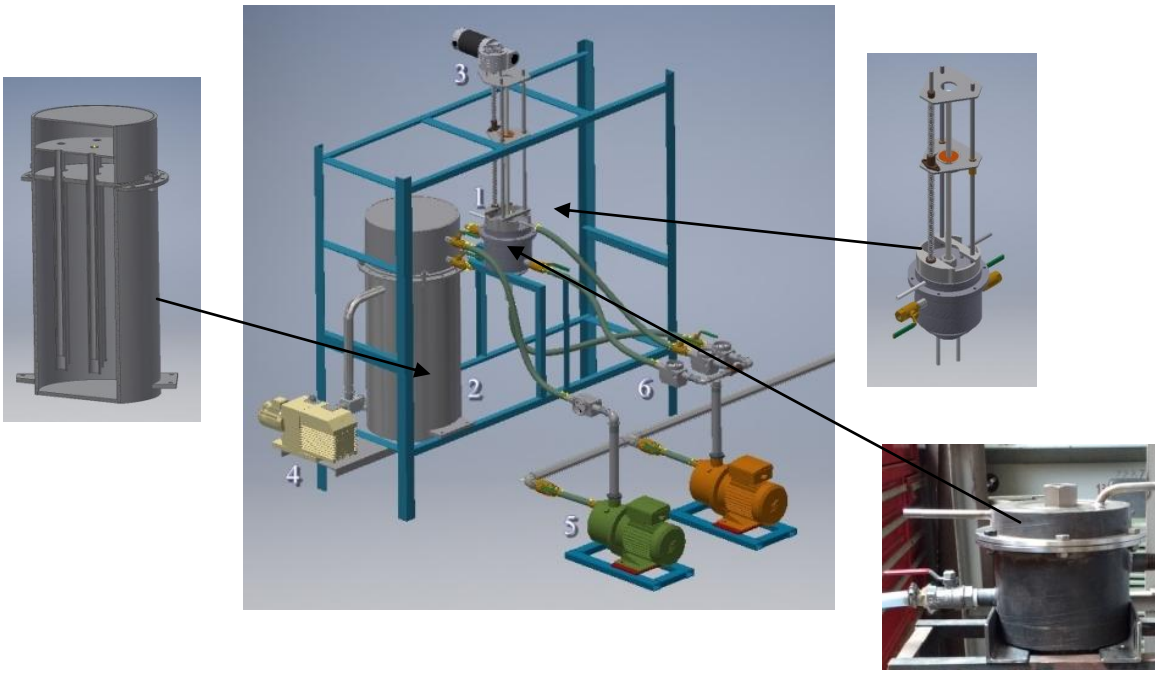
Ti/TiAl eksperimentālās iekārtas reaktora moduļa stends.

Kā jau minēts Progresa ziņojumā-2, lai izpētītu un atrastu optimālus režīmus titāna pilienu (kuri atdalījušies no elektroda), caurplūdei cauri izkausētam un uzkarsētam līdz 1400°C kušņu (flux) slānim un to nosēšanos uz titāna aizmetņa virsmas, kas atrodas zem izkausētās kušņu - *flux* kārtas izstrādāts reaktora moduļa stenda tehniskais projekts, zīm. 1.1.

Reaktora moduļa stenda galvenās sastādaļas ir:

- reaktors, poz.1,
- kondensators, poz.2,
- elektroda piedziņas mehānisms, poz.3,
- vakuumsūknis, poz. 4,
- ūdens sūkņi, poz.5 un
- caurteces mērītāji, poz.6.

Galvenās ierīces un mezgli tiek un projekta gaitā tiks uzmontēti uz speciāla rāmja.



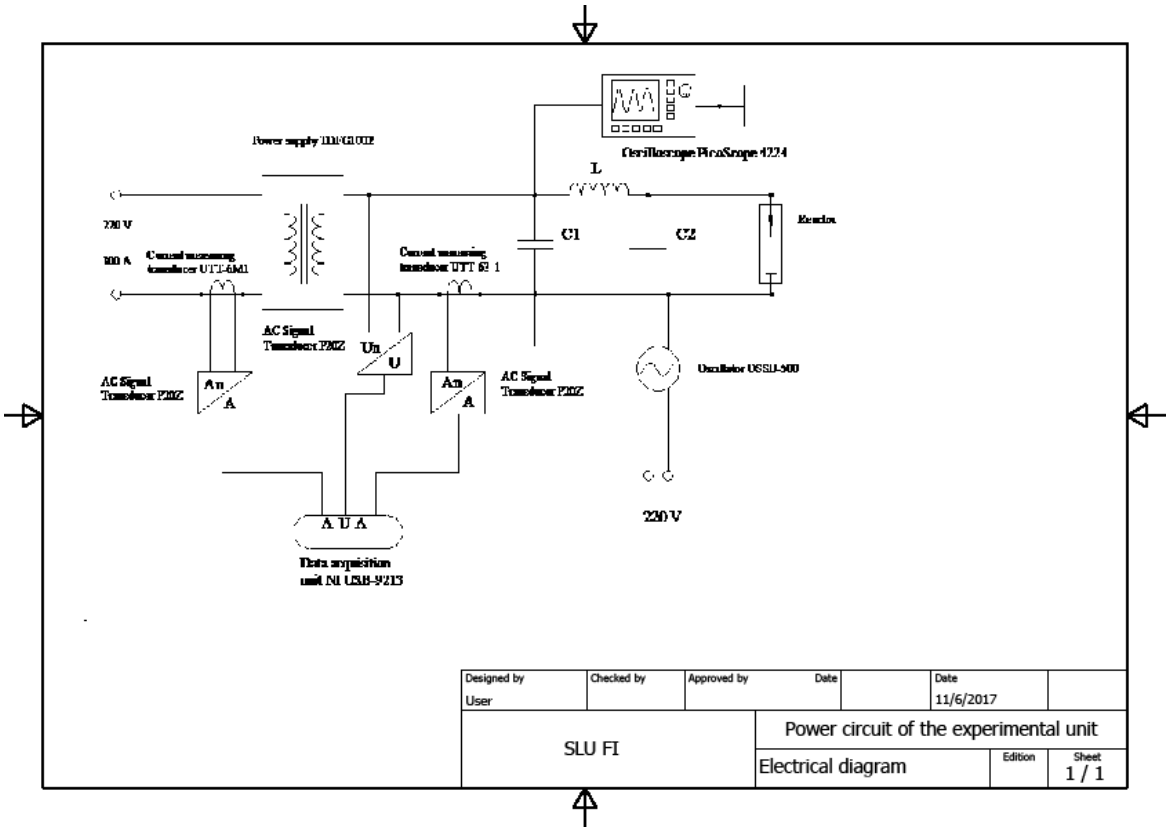
Zīm.1.1. Ti/TiAl eksperimentālās iekārtas reaktora moduļa stends.

Projekta 3. etapā paredzēto darbu izpildes laikā turpinājās Ti/TiAl eksperimentālās iekārtas reaktora moduļa stenda montāža, kuras rezultātā paveikts sekojošais:

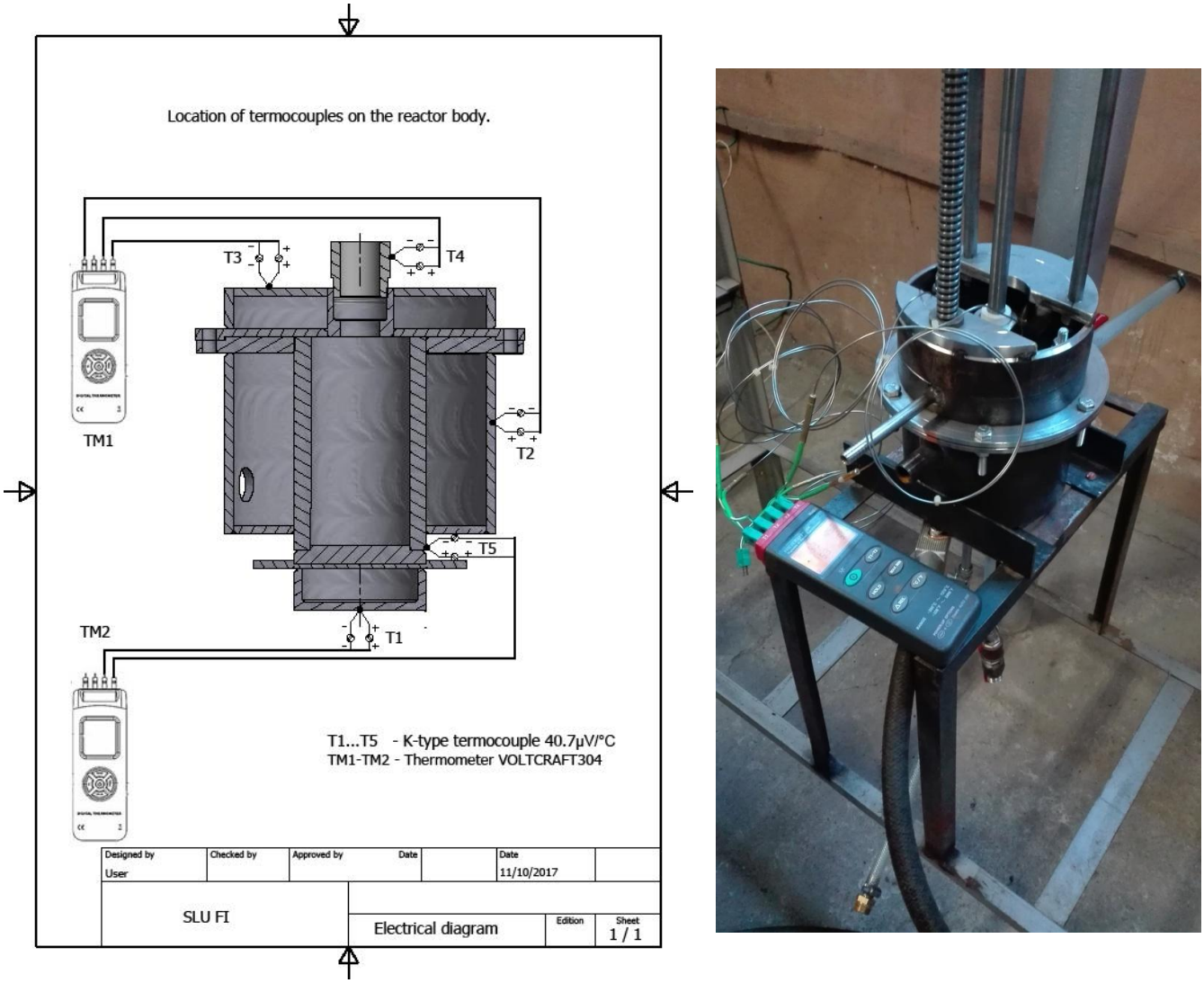
- uz reaktora moduļa uzmontēts elektroda piedziņas mehānisms, zīm. 1.2.;
- reaktora modulis kopā ar piedziņas mehānismu pārbaudīts uz vakuumu un spiedienu (15bari);
- elektroda barošanai renovēts 10 kW barošanas bloks (transformators), zīm. 1.3;
- izstrādāta reaktora modula barošanas principiālā shēma, zīm.1.4.;
- transformators pieslēgts elektriskajam tīklam un veikta tā darbības pārbaude tukšgaitā;
- lai sagatavotu stendu eksperimentiem ar elektrodu un kontrolētu reaktora sastāvdaļu temperatūru, reaktora korpusam uzmontēts definēts skaits termopāru, zīm.1.5.;

Sekmīgai eksperimentu veikšanai ar titāna elektrodu vēl nepieciešams izstrādāt un samontēt reaktora korpusa un tā atsevišķu sastāvdaļu dzesēšanas sistēmu.

Zīm.1.2. Reaktora moduļa stenda kopskats. Zīm.!.3. Barošanas bloks (10kW)



Zīm.1.4. Reaktora moduļa barošanas principiālā shēma.



Zīm.1.5. Reaktora modulis aprīkots ar definētu termopāru skaitu.

Aktivitāte Nr.2. Eksperimentālā validācija.

2.1. Pirmie eksperimenti un to mērķis.

Projekta 3.etapa darbu izpildes laikā turpinājās iespējamo kušņu īpšību analīze un iespēja tos izmantot Ti pārkausēšanas procesā, kā arī iegūto termovakuumkrāsnī paraugu analīze ar mērķi izpētīt kā titāns filtrējas cauri kušņu slānim.
Elektrosārņu pārkausēšana (ESP) ir sekundārs metālu rafinēšanas process. Izmantojamā elektroda ESP ar ūdeni dzesējamā kristalizatorā plaši izmanto rūpniecībā.
Šajā procesā sārņu slānim ir divas svarīgas funkcijas – tas kalpo gan kā galvenais siltuma avots, gan kā būtiskākais ķīmiskā sastāva regulēšanas līdzeklis. Sārņiem ir arī vairākas palīgfunkcijas.

Sacietējot uz kristalizatora sieniņām, tie novērš tiešu saskari starp izkausēto metālu un kristalizatora materiālu, izolējot metālu gan termiskā, gan elektriskā ziņā no kristalizatora un līdz ar to, aizsargājot metālu no oksidēšanās. ESP procesā sārņu vanna tiek uzkarsēta un izkausēta ar elektriskās strāvas palīdzību, kas plūst no elektroda uz dzesējamo pamatni. Kad sārņu vannas temperatūra pārsnierdz rafinējamā metāla kušanas temperatūru, elektrods sāk apkust. No elektroda gala tekošie šķidrā metāla pilieni nokļūst sārņu vannā, veidojot uz pamatnes metāla vannu, kas pakāpeniski sacietē. Rafinēšana notiek metāla un sārņu savstarpējas reakcijas procesā, kas norit trīs stadijās:

- veidojoties pilienam elektroda galā;
- izejot metāla pilienam caur sārņiem;
- pie robežvirsmas sārņu vanna/metāla vanna.

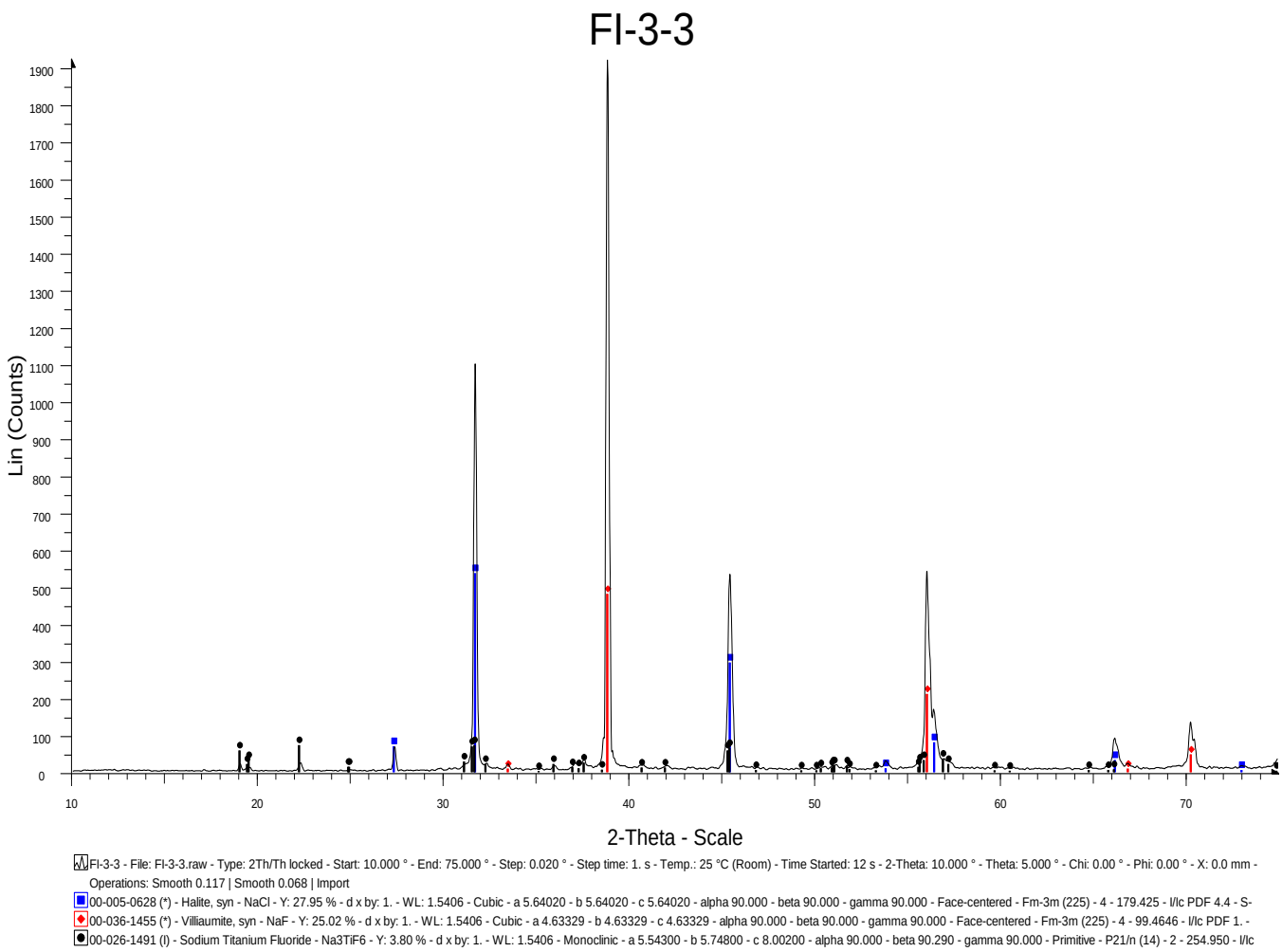
Sārņu sastāvdaļu izvēle.

1. ESP sārņu galvenā sastāvdaļa parasti ir CaF_2, CaO, MgO, SiO_2 un Al_2O_3. Šiem materiāliem piemīt stabilitāte augstās temperatūrās, t. i. zems tvaiku spiediens. Minētās vielas būtībā nosaka sārņu fizikālās un ķīmiskās īpašības.
2. Mazāk nozīmīgu sārņu sastāvdaļu (<10%) izvēle vajadzības gadījumā uzlabo sārņu ķīmiskās īpašības. Kā šādas piedevas izmanto, piemēram, metālu fluorīdus (MgF_2 vai BaF_2), stabilus oksīdus (BaO vai ZrO_2), nestabilus oksīdus (TiO_2, SiO_2 u.c.), metālu karbīdus, nitrīdus, silicīdus, borīdus un citus savienojumus.

Izvēloties sārņu sastāvu ESP procesam tiek ievērotas sekojošas pamatprasības:

- sārņu sastāva kušanas temperatūrai jābūt zemākai par metāla kušanas temperatūru, maisījumam jābūt stabilam procesa darba temperatūrā;
- sārņu maisījumam jāvada elektrība;
- sastāvam jāgarantē vēlamo ķīmisko reakciju norisi;
- sārņu ķīmiskajai aktivitātei jāatbilst gala produkta vēlamajai tīrības pakāpei un ķīmiskajam sastāvam.
- sārņu maisījumam jābūt ar atbilstošu stigrību procesam paredzētajā temperatūrā.

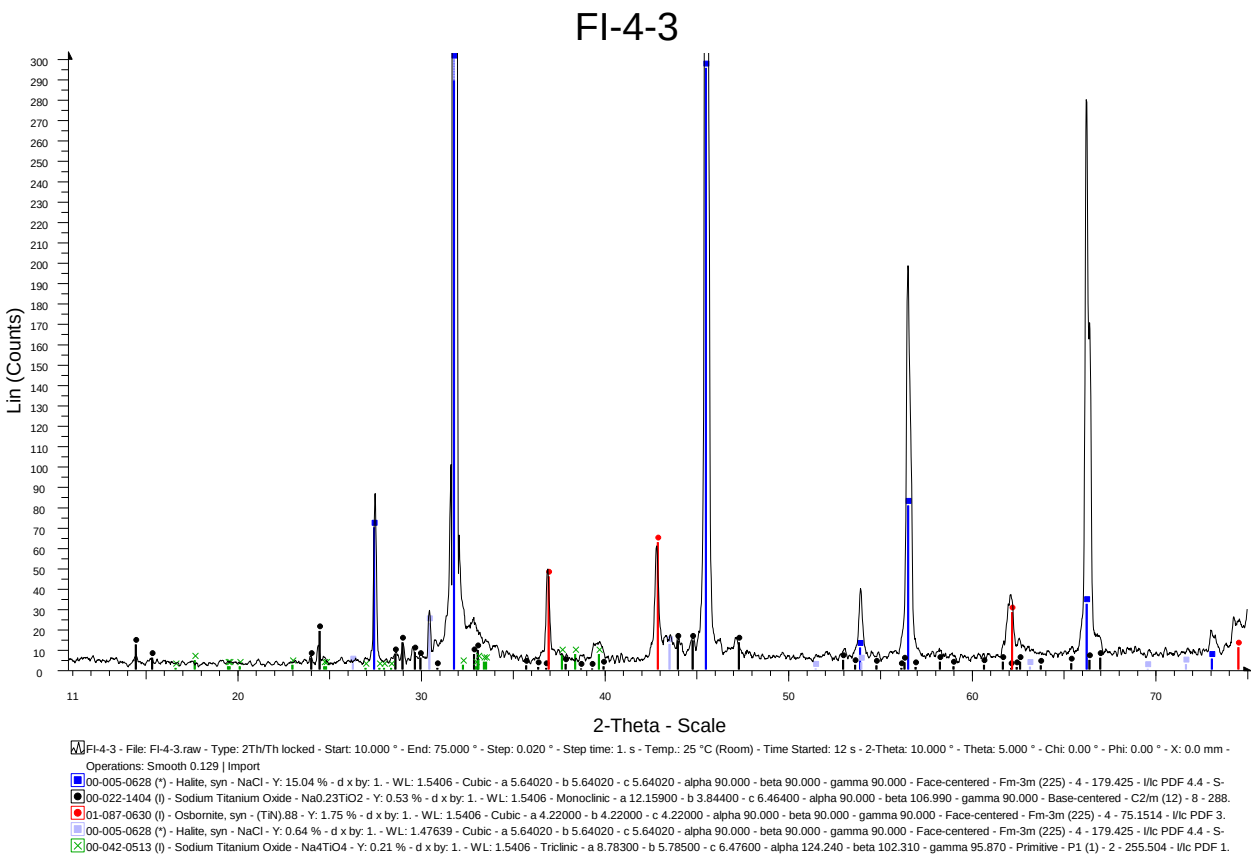
Svarīga loma ir arī tādiem raksturlielumiem, kā siltumvadītspēja, stigrība un virsmas spraigums.
Fluorīdu – oksīdu sārņu sistēmas, kas ir visuniversālākās lietošanai ESP procesos, satur CaF_2 un CaO; CaF_2 un Al_2O_3; CaF_2, CaO un Al_2O_3; CaF_2, MgO un Al_2O_3. Tādējādi ESP procesā metāls tiek izkausēts un attīrīts, ejot caur vannu ar izkausētiem sārņiem uz fluorīdu bāzes.
Hantera procesa pamatā ir titāna tetrahlorīda termiska reducēšana , izmantojot nātriju. Reakcijas gala produkts ir tīrs titāna pulveris un nātrija hlorīds. Tā rezultātā, kombinējot Hantera metodi ar ESP procesu, sārņu sastāva izvēli nosaka gan procesa fizikālie parametri, gan īpašas prasības sārņu sistēmas izejas komponentu sastāvam un tīrības pakāpei, lai izvairītos no metāla piesārņošanas, tam ejot caur sārņu vannu. Nepieciešams arī ņemt vērā NaCl klātbūtni sārņos – tā daudzums pieaug, reducējot titānu (IV) līdz metālam.
Hantera procesa beigu stadijas sastāvam atbilstošā modeļsistēmā - reakcijas galaprodukti (attiecība maisījumā Ti : NaCl =1:4,5) keramiska tīģeļa augšējā daļā un sārņi uz NaF bāzes tīģeļa apakšējā daļā – pētīts sārņu ķīmiskais sastāvs pēc 1 stundu ilgas parauga apstrādes pie 1025^0C argona atmosfērā (objekts 1). Saskaņā ar veiktajiem rentgenogrāfiskajiem pētījumiem , (zīm. 2.1.) sārņos kopā ar NaF un NaCl konstatēts arī Na_3TiF_6. Atsevišķos objekta paraugos piemaisījumu veidā atrasti arī produkti, kas veidojušies sistēmas komponentu mijiedarbībā ar skābekli, kas nav pilnībā izvadīts no sistēmas, $Na_4Ti_5O_{12}$ un Ti_2O_3, kā arī ar tīģeļa materiālu - $NaAlSiO_4$.



Zīm.2.1. Modeļparauga 1 sārņu parauga rentgenogramma.

Nomainot tīģeļa materiālu ar nerūsējošo tēraudu un kušņu (NaF) slāni tīģeļa apakšējā daļā ar tīru NaCl, pārkausēšanas procesā pie 1050^0C 30 minūšu laikā tika iegūts objekts 2, kurš parādīts zīm.2. 2. No dažādām kušņu zonām ņemto paraugu rentgenogrāfiskā fāžu analīze uzrādīja tādu piemaisījumu kā nātrija titanāti un dažādas stehiometrijas titāna oksīdi, kā arī TiN klātbūtni, zīm.2.3. Objektā atrasti arī produkti, kas radušies titāna un tīģeļa materiāla mijiedarbības rezultātā skābekļa klātbūtnē, kā arī tīģeļa materiāla oksidēšanās produkts - Fe_2O_3.

Att.2.2. Objekta 2 gareniskā griezuma attēls.



Zīm. 2.3. Modeļparauga 2 sārņu parauga rentgenogramma.

Veikto eksperimentu un paraugu analīzes rezultātā izpētīts sārņu fāzu sastāvs pēc to pārkausēšanas vakuumkrāsnī argona atmosfērā. Tā kā eksperimentos tika izmantots tehniskais argons, kurā ir ievērojams skābekla un slāpekļa procents, neizdevās iegūt tīra titāna aizmetni. To apliecina kušņos fiksētā skābekļa un slāpekļa savienojumu klātbūtne. Tas nozīmē, ka turpmākie pētījumi jāveic vakuuma, vai arī paaugstinātas tīrības argona apstākļos.

Aktivitāte Nr.3. Mērījumi, modelēšana un raksturošana

Sākta zinātniskās literatūras meklēšana un apzināšana par industriālo sārņu termofizikāliem raksturlielumiem un to atkarībām no eletrosārņu sistēmas termodinamiskiem parametriem. Sākta iegūto datu apstrādāšana un apkopošana skaitlisko modeļu parametrizācijai. Sākta iepriekšējā atskaites periodā iegūto zinātnisko rezultātu apkopošana, analīze un noformēšana, vizuālā materiāla sagatavošana, zinātniskās publikācijas sagatavošana un rediģēšana atbilstoši recenzentu atsauksmēm. Iegūtie zinātniskie rezultāti noformēti un prezentēti starptautiskajā zinātniskajā konferencē "Materials Science and Applied Chemistry, MSAC 2017

Aktivitāte Nr.4. Zināšanu un tehnoloģijas pārnese

Iegūtie rezultāti, literatūras avoti, darbs projekta aktivitātēs regulāri apspriesti projekta semināros. Notiek ziņojumu sagatavošana starptautiskām konferencēm lai nodrošinātu projekta iznākuma rādītāja Nr. 13 „Citi pētījuma specifikai atbilstoši projekta rezultāti (t.sk. dati), kas

papildina rezultātu rādītājos Nr. 2., 3.1., 4., 5. minētos rezultātus" sasniegšanu. Projekta pirmo 6 mēnešu rezultāti tika prezentēti 2 zinātniskos referātos konferncē „Modelling for Materials Processing" MMP-2017. (Pielikums 1,3), kā arī ziņoti „Materials Science and Applied Chemistry" MSAC-2017 konferencē (1 referāts, Pielikums 2).

5.Secinājumi.

- Bāzējoties uz pirmajos divos etapos izstrādāto stenda tehnisko dokumentāciju un uz speciālā rāmī iemontētā reaktora modeļa, uzmontēts elektroda piedziņas mehānisms.
- Reaktora modelis kopā ar elektroda piedziņas mehānismu pārbaudīts uz spiedienu robežās $p = 5x10^{-2}$ Pa – 1,5 MPa (vakuums – spiediens).
- Rekonstruēts elektroda barošanas bloks (10kW), un veikta tā profilakse.
- Barošanas bloks pārbaudīts tukšgaitā un pieslēgts reaktora moduļa elektrodam..
- Turpinājās otrajā etapā termovakuumkrāsnī iegūto paraugu rentgena – fāžu un rentgena – fluorescenses analīze. Konstatēts, ka notiek daļēja titāna filtrācija cauri kušņu slānim.Tomēr process (eksperiments) bija daļēji ne korekts, jo tika izmantots tehniskais argons, kurš satur lielu skābekļa un slāpekļa procentu.
- Turpinājās Ti/TiAl eksperimentālās iekārtas tehniskā projekta izstrādāsana.
- Turpinājās literatūras analīze, lai apzinātu titāna ražošanas procesa matemātiskā modeļa formulēšanu.;
- Prezentēti trīs referāti starptautiskās konferencēs.

Problēmas. Arvien vēl Iepirkumi!

Plāns (orientējošs)
1. Pabeigt Ti/TiAl eksperimentālās iekārtas tehniskā projekta izstrādāšnu
2. Sagatavot titāna reaktora modeļa stendu eksperimentu veikšanai ar elektrodu
3. Veikt titāna filtrācijas eksperimentus reaktora modelī cauri kušņu sļānim,izmantojot titāna elektrodu.
4. Veikt iegūto paraugu rentgena –fāžu un rentgena – fluorescenses ķīmiskā sastāva analīzi.
5. Turpināt termodinamiskos aprēķinus un hidrodinamikas modelēšanu.
6. Sagatavot rakstu publicēšanai..

Pielikums Nr.1.

VIII International Scientific Colloquium
Modelling for Materials Processing
Riga, September 21 - 22, 2017

A feasibility study for high-temperature titanium reduction from $TiCl_4$ using a magnesiothermic process

S. Ivanov, D. Zablockis

Abstract

Realization of the process of titanium production by magnesium thermal reduction from titanium tetrachloride at a temperature higher than that of the modern industrial process using a reactor produced from a high-temperature niobium alloy.

Introduction

Titanium is the most common metals and has a unique combination of properties. Due to the high specific strength, refractoriness and heat resistance, it is widely used in the aerospace industry, shipbuilding industry, nuclear industry. However, the complex composition of the titanium-containing minerals and a high affinity of titanium to oxygen to create difficulties in obtaining pure titanium, necessitating a plurality of process stages, and complex hardware and flow chart implemented in the industrial production of titanium with magnesium (Kroll process). Broad effective use of titanium is limited by its high cost. Numerous attempts industrial implementation of other ways of manufacturing of titanium were unsuccessful.

Chlorination of enriched titanium ore yielding titanium tetrachloride and its thermal reduction to metallic titanium by magnesium is the basic modern industrial method of titanium production. Steel retorts are used in the production. When interacting with titanium, iron and nickel in steels form a liquid eutectic at high temperatures. These materials are washed out, the sponge titanium is polluted (contaminated) and the walls of the retort become flimsy (exhausted). Therefore, the heating of the retort is limited to 900 °C. The titanium, which contacts with the steel walls of the equipment, is contaminated by the material of the walls; that is why it undergoes regeneration or is used as a low-grade material. After multistage processing of metallic titanium, only 10-15% of pure titanium is produced from this titanium raw material.

About 70 reactions are possible in the system $TiCl_4$(Ti(IV)) -$TiCl_3$ - $TiCl_2$(Ti(II)) - TiCl - Ti - Mg – MgCl - MgCl2(Mg(II)). The following ones are selected from the point of view of thermodynamics and kinetics (see Fig. 1) [1]. The reduction takes place as intermediate stages of the formation of titanium lowest chlorides. The first, most possible stage is the reduction of $TiCl_4$ vapors by magnesium to $TiCl_2$ because this demands the collision of only two molecules of the initial reagents. The formation of lowest chlorides is also possible as a result of the secondary reactions of chlorides with Ti. A complex multi-phase contribution of the components to the reaction takes place. To obtain the desired result, it is necessary to understand not only the kinetics of the directly reacting molecules, but also their transport into the region of reaction and the removal of the reaction products from it, and then to correctly realize the process.

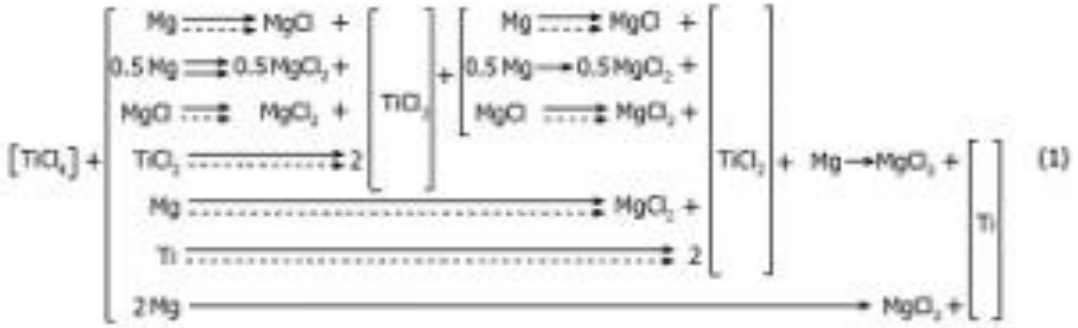


Fig. 1. Schematic presentation of the desired reactions in thermodynamics and kinetics (solid arrows – condensed phase, dashed arrows – vapor-gas phase).

Theoretical studies [2] show that the temperature range 1200 – 1400 °C is more beneficial for the reduction to metallic titanium. The development and realization of new highly effective methods of thermal reduction of titanium by magnesium are determined by the technological and design features of the process when the interaction of Ti(IV) with magnesium would occur at a higher temperature if compare with that of the existing process and under more beneficial conditions.

1. New reactor

The use of niobium alloy makes it possible to considerably increase the temperature in the reactor and to carry out the reduction process in the optimal temperature range. The temperature increase in the reactor offers the possibility of rapid removal of magnesium chlorides by diffusion into the condenser (Fig. 2). The removal of magnesium chlorides, which comprise more than 90% of the reaction products, makes more working space in the reactor.

The IPUL team has accumulated experience with NbZr contours with lithium at high temperature (>1000°C) in a vacuum [3]. The NbZr alloy is weldable and therefore suitable for the production of a retort for magnesiothermic reduction of titanium tetrachloride at temperatures 1200-1400 °C. In 2007 the IPUL team conducted a preliminary experiments on magnesiotheermic reduction up to 1100 °C in a small reactor made of NbZr alloy. Cerrosive degradation was not observed.

The temperature ranges exceeding 1000 °C have not been studied in detail experimentally. We make attempts to predict how to utilize the advantages of the reaction occurring in the reactor at 1150 °C (this temperature is applicable for niobium in magnesium [4]) and how to realize the process using special equipment, i.e. high-temperature, quick-operating valves and gates or shutters which will make it possible to control the process such that it would take place predominantly in the gas phase. The control implies a dose supply of reagents and the removal of volatiles after the reaction, making room for another reaction. In this case, the working space will be reduced only due to the titanium remaining in the reactor. Since in the gas phase titanium is formed as powder [5], then, apparently, it will be possible to design a reactor with the periodic titanium powder spilling through the opening channel into a separate tank (vessel) outside the reactor and the furnace. Then the thermal reduction of titanium by magnesium can be assumed continuous.

1.4. Scenario of the reactor operation.

1 – vacuum, reactor temperature 1150 °C
2 - 0.333 g supply / 10 L-bucket with magnesium; the pressure in the reactor increases to 0.163 bar
3 - Ti(IV) injection of 1.297 (g/bucket). The reaction takes place. Very quickly. With heat release.
4 - 1.302 (g/bucket) of magnesium chloride vapors and 0.327 (g/bucket) of solid titanium are formed in the reactor. The pressure in the reactor is 0.137 bar.
5 – the outlet valve (gate) is open which connects the reactor with the cold evacuated chamber with the temperature 720 °C (the vapor pressure is 48 Pa) to collect magnesium chloride
6 – the cycle is completed after the valve is shut (closed). The pressure in the reactor is 50 Pa; then follows p.1.

The quantity of titanium per cycle is equal to a cube with the edge 0.47 cm. The procedure distribution in time for one cycle is illustrated in the diagram in Fig. 2. The cycle duration includes the time of evaporation of the supplied magnesium, the time of the reaction, the precipitation of fine dispersed titanium on the walls, and the time of the distillation of volatiles into the condenser. Titanium is periodically spilled through the bottom hole by opening the shutter (not shown in Fig. 2). Powder titanium can undergo electroslag remelting to produce ingots of titanium alloys.

Conclusions

The plant with 50 constantly operating $10m^3$ reactors will produce 18.95 thousand tons of powdered pure titanium throughout the year. The income from the sale of titanium at the average market price is estimated at $ 0.379 billion. This perspective justifies the cost of expensive research.

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References

[1] Garmata V.A., et al. Titanium. (Moscow, Metallurgiya, 1983, 559 p.).
[2] Yu.N.Olkhov, S.V.Ogurtsov et al. Thermodynamics of the titanium redox reaction from titanium tetrachloride by magnesium and the choice of optimal ways to intensify the titanium production. In: Investigations in Titanium Chloric Metallurgy (Moscow, Metallurgiya, 1969, 302 p.).
[3] Ivanov S.L., Foliforov V. M., Platacis E. et. al. Special features of Electromagnetic Pump Investigations for Space Nuclear Reactors, 2nd International Conference of Energy Transfer in MHD-flow. Aussois-France,1994, 643-650.
[4] A.V. Byalobzheskiy, M.S.Tsirlin, B.I.Krasilov High-temperature corrosion and the protection of super-refractory metals. Moscow, Atomizdat, 1977.
[5] P.C. Turner, A. Hartman, J. S. Hansen, S. J. Gerdemann. Low cost titanium - myth or reality. DOE/ Albany Research Center - 2001-086

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Phase composition and nanomorphology of tungsten oxide nanoflakes produced via a pyrolytic process

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Keywords: tungsten oxide, nanoflakes, nanoparticles, liquid extraction, pyrolysis

Abstract. The chemical synthesis is a leading route for the purposeful design of nanomaterials, whereas the tungsten oxides are employed in a variety of special applications. The production of nanomaterials by traditional synthetic methods is still a cumbersome multistep process. Here we propose an improved method to produce tungsten oxide nanomorphologies via a pyrolytic process. A tungsten-containing precursor was prepared by liquid extraction using n-trioctylamine $(C_8H_{17})_3N$ solution in toluene. We have shown that the conditions of thermal treatment of the W-based precursor determine the crystalline structure and nanomorphology of the final product. Monoclinic WO_3 nanocrystallites are produced conducting the pyrolysis above 450 °C. The proposed method is a facile and versatile route to produce and control the phase composition and morphology of tungsten oxide-based nanomaterials.

Introduction

Tungsten oxides possess a combination of properties (photosensitivity, electron mobility, stability in acidic solutions) that make them suitable semiconductor metal oxides (SMO) for a variety of applications: electrochromic [1,2] (e.g. smart windows [3] and displays [2,4]) components change their optical properties due to electric current; efficient photocatalytic systems [5,6], photoanode materials with high incident photon-to-current conversion efficiencies for solar energy driven photoelectrochemical water splitting to produce molecular hydrogen [1][7-9] - a key technology for "green" society. SMO-based chemical sensors [10-16] reliably detect volatile organic - acetone [10], alcohol [10,13] - or gaseous (e.g. nitrogen oxides (N_2O, NO, NO_2 [11-12,16-17]) [17], NH_3 [14], H_2S [13], H_2 [18]) adsorbates. Nanostructured forms of SMOs, incl. WO_3, are exploited to fabricate such devices and to increase their efficiencies, sensitivity and achieve fast response/recovery due to an enhanced surface-to-volume ratio [9,18]. Thus, the rational design of the nanocrystalline morphology [19,20] and phase composition in the size range below <50 nm is key to superior performance. Tungsten (VI) oxides are produced by hydrothermal [8] or solvothermal [11] reaction, solution precipitation via hydrolysis of tungstate salts under acidic conditions [21] or sol-gel processing, which is a versatile technique starting from tungsten alkoxide [15] or tungstic acid [1,4,7] precursors. The cost and purity of the precursors is a key concern for nanoparticle synthesis. The raw materials (e.g. tungstates) may contain additives leading to unclear effect on morphologies and the intrinsic formation mechanisms. Frequently, a prolonged calcination to form WO_3 with high crystallinity - a prerequisite for many applications – leads to suboptimal morphology and an overall increase of the particle size. The extraction-pyrolysis method (EPM) is a viable alternative to the sol-gel route to produce metal oxide nanomaterials [22-24] (incl. SMOs) via a two stage process: metal extraction from the aqueous phase into the organic one and the subsequent pyrolytic decomposition of the produced metal organic precursor. The refinement, quite exhaustive if necessary, of target components is affected during the extraction stage. The pH value, tungsten

concentration and storage time of the aqueous solution determine the composition of the forming and extracting compounds [25]: alkaline (pH > 8) solutions of tungstates contain an equilibrium mixture of monotungstate ions $[WO_4]^{2-}$ and $[HWO_4]^-$, which polymerize upon acidification forming complex polytungstate anions, e.g. hexatungstate ions $[HW_6O_{21}]^{5-}$ appear at pH 8-6. The salts of ternary amines (e.g. n-trioctylamine $(C_8H_{17})_3N$; Oct_3N) efficiently extract tungsten from weakly acidic (pH 2-3) solutions containing polymeric anions of tungsten and are employed for industrial production of pure tungsten compounds in hydrometallurgy [26]. The extraction of anionic forms of metals by trioctylammonium chloride $[Oct_3NH]^+Cl^-$ into the organic phase is achieved by anion exchange and formation of ionic associate with trioctylammonium $[Oct_3NH]^+$ [27]. Previously [23] we have shown that the pyrolytic decomposition of metal-containing extracts is a viable method to produce metal oxide nanopowders and nanocomposites. Herein, we report a study on the formation, nanomorphological and phase transformations of tungsten oxide nanoflakes produced via a pyrolytic treatment of a tungsten-containing extraction system, i.e. a solution of tungstate trioctylammonium in toluene.

Experimental methods

Initially, a weakly-alkaline aqueous solution of 0.25 M Na_2WO_4 was prepared for extraction. The pH was adjusted to 7.5 by dropwise addition of aqueous solution of hydrochloric acid. An organic solution of 0.6 M Oct_3N in toluene was prepared for use as the extractant. Initially, Oct_3N was converted into a hydrochloric salt $[Oct_3NH]^+Cl^-$ by shaking it for 5 min with an equal volume of aqueous solution of 1M HCl. After the phases were allowed to separate for 2 hours, the aqueous phase was removed. Then equal volumes of aqueous solution of Na_2WO_4 and toluene solution of $[Oct_3NH]^+Cl^-$ were mixed in a separation funnel, the time of phase contact was 10 min. After complete stratification and removal of the aqueous phase followed by filtration, a tungsten-rich precursor was produced.

The concentration of tungsten in the precursor solution was determined photometrically using ammonium thiocyanate as described elsewhere [25]. To this end an aliquot of the precursor was taken followed by reextraction into an aqueous phase by a 0.5 M solution of NaOH. The thermal stability of the produced precursor was studied by thermal gravimetric analysis (TGA) using the STA PT1600 (LINSEIS). The sample was heated in static air from ambient temperature to 700 °C at a rate of 10 °C/min.

The tungsten oxide-based nanomaterials were produced by thermal treatment of the precursor solution: heating it from ambient to a final temperature T (400 °C÷700 °C) in a muffle furnace in air followed by annealing for 30-90 minutes. The sample was then allowed to cool under ambient conditions. The phase composition of the final product was studied by the X-ray diffraction (XRD) method (diffractometer D8 Advance, Bruker Corporation) with CuK_α radiation (λ = 1.5418Å). The mean size of the tungsten trioxide crystallites was determined from the half-width of the diffraction maxima by the Scherrer method (EVA software). The products of pyrolysis were additionally investigated by infrared (IR) absorption spectroscopy (EQUINOX 55, Bruker with KBr pellets) and transmission electron microscopy (TEM) (FEI Technai G2 F20 operating at 200 kV).

Results and discussion

The photometrical analysis of the reextract shows that the concentration of the metal in the extract was 0.25 M, evidencing that trioctylammonium chloride efficiently extracts tungsten into the organic phase from a weakly alkaline solution at the above-described conditions. Presumably, tungsten is extracted from the aqueous phase both as monotungstate ions and tungsten-containing polymeric anions.

the m-WO_3 crystallites increases from approx. 20 nm (S3-500 °C) to 45 nm (S4-700 °C) with the temperature of the pyrolysis.

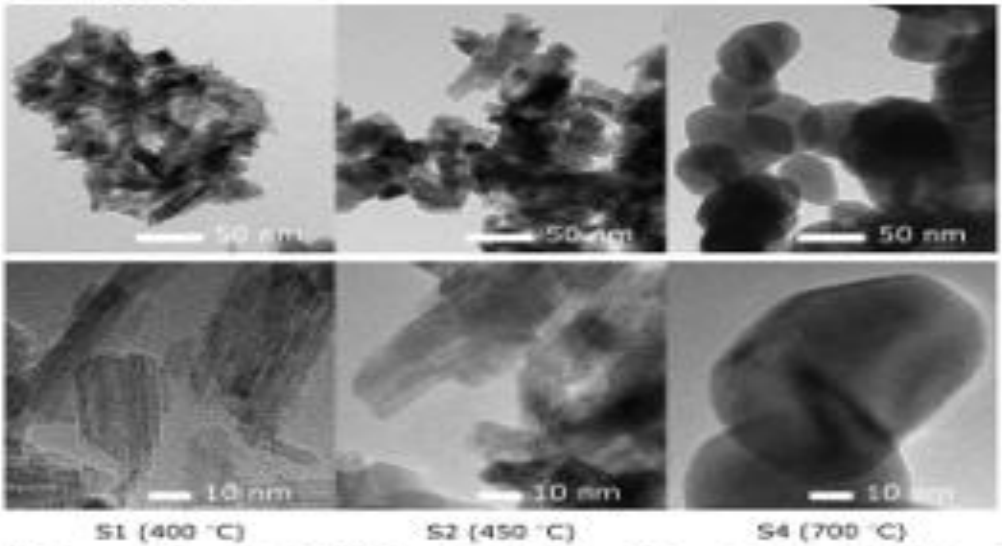

Fig. 2. TEM images of samples S1/S2/S4 produced by pyrolytic synthesis at 400, 450 and 700 °C.

The morphology and crystal structure of samples S1 (400 °C)/S2 (450 °C)/S4 (700 °C) according to TEM is shown in Fig. 2, indicating the formation of tungsten oxide nanoflakes at 400 °C. HRTEM analysis indicates good crystallinity of the nanoflakes. The pronounced peak in the XRD pattern of sample S1 (Fig. 1, right) may be associated with the strong anisometry of these nanocrystallites due to preferred growth along a single crystallographic direction. Increasing the temperature of thermal treatment to 450 °C initiated the coalescence of the nanoflakes into larger faceted crystals 20-70 nm long and 15-20 nm in diameter (shown schematically in Fig. 3, left). The thermal treatment at 700 °C produced slightly elongated round-shaped particles of approx. 40 nm resulting in a fully developed triplet structure in the XRD pattern of sample S4 (Fig. 1, right)

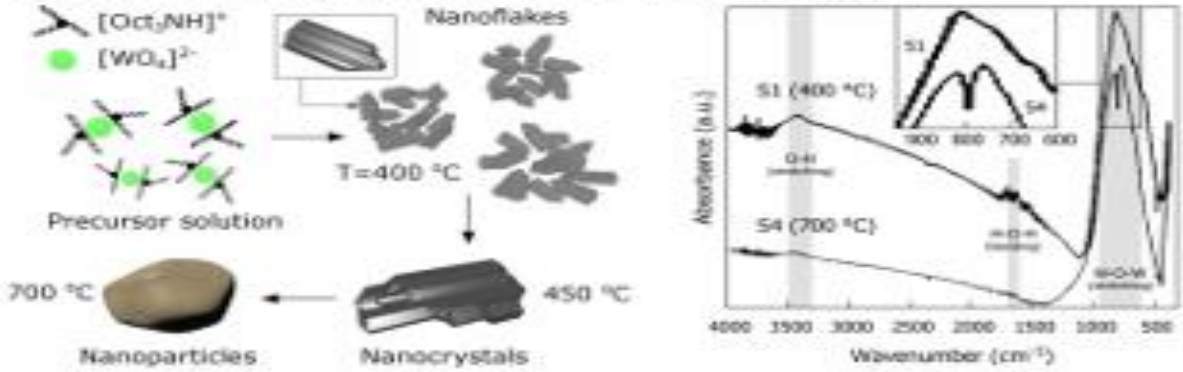

Fig. 3. Left: Schematic representation of the presumed nanocrystal formation process and morphological evolution. Right: FT-IR spectra of samples S1 and S4 produced by pyrolytic synthesis at 400 and 700 °C.

The infrared absorption spectra of the samples produced at the lowest S1 (400 °C) and highest S4 (700 °C) temperatures are shown in Fig. 3. The 600-950 cm^{-1} region corresponds to the W-O-W stretching vibrations [28][29]. The weak peaks in the regions approx. 3300-3500 cm^{-1} and 1600-1700 cm^{-1} are associated with the O-H stretching and H-O-H bending modes from crystallization water in S1 [29]. The intensity of these peaks decreases with increasing temperature of thermal treatment. In the 600-900 cm^{-1} region S1 (400 °C) shows one strong peak at approx. 800 cm^{-1} whereas S4 (700 °C) displays two peaks at approx. 815 cm^{-1} and 755 cm^{-1}, which may indicate the previously discussed difference in the crystalline structure of the tungsten oxides. Here, the spectrum of S4 coincides with the IR spectrum of *m*-WO_3 reported by Daniel et al. (1987) [28]. Note that no presence of organic admixtures has been found in either sample.

Conclusions

In summary, we described a facile and chemically clean inorganic route based on a pyrolytic treatment of trioctylammonium tungstate produced by liquid extraction to synthesize tungsten oxide nanomaterials. Exploiting the key parameters of the precursor decomposition we demonstrate the ability to exert selective morphological control by simply varying the temperature of the pyrolytic synthesis, whereby the WO_3 nanoparticle evolves via formation of low-dimensional nanoflakes and their coalescence into faceted nanocrystals accompanied by the enlargement of the WO_3 crystallites. Overall, the proposed synthetic approach is a cost-effective strategy for monophase *m*-WO_3 with size ranging from 20 to 50 nm as prospective candidates for electrochromic, photochemical and electrochemical (incl. sensing) applications. Further studies should be directed toward exposing the growth mechanism of the nanocrystals for improved morphological modification.

Acknowledgments

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References

[1] C. Santato, M. Odziemkowski, M. Ulmann, J. Augustynski, Crystallographically Oriented Mesoporous WO_3 Films: Synthesis, Characterization, and Applications, JACS 123 (2001), 10639-10649

[2] S.K. Deb, Opportunities and challenges in science and technology of WO_3 for electrochromic and related applications, Sol. Energ. Mat. Sol. C. 92 (2008), 245-258

[3] C. Bechinger, S. Ferrere, A. Zaban, J. Sprague, B.A. Gregg, Photoelectrochromic windows and displays, Nature 383 (1996), 608 - 610

[4] G. Leftheriotis, S. Papaefthimiou, P. Yianoulis, A. Siokou, D. Kefalas, Structural and electrochemical properties of opaque sol–gel deposited WO_3 layers, Appl. Surf. Sci. 218 (2003), 276-281

[5] R. Abe, H. Takami, N. Murakami, B. Ohtani, Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-Loaded Tungsten Oxide, JACS 130 (2008), 7780-7781

[6] Zh.-G. Zhao, M. Miyauchi, Nanoporous-Walled Tungsten Oxide Nanotubes as Highly Active Visible-Light-Driven Photocatalysts, Angew. Chem. Int. Ed. 47 (2008), 7051–7055

[7] C. Santato, M. Ulmann, J. Augustynski, Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films, J. Phys. Chem. B 105 (2001), 936-940

[8] S.J. Hong, H. Jun, P.H. Borse, J.S. Lee, Size effects of WO_3 nanocrystals for photooxidation of water in particulate suspension and photoelectrochemical film systems, Int. J. Hydrogen Energy 34 (2009), 3234-3242

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Insight at the electroslag process for better morphology of titanium deposits

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Abstract

Kroll process for more than 50 years is a titanium-based production technology. The primary product of titanium extraction is a titanium sponge, which requires complicated processing. A variation of the Kroll process for the producing titanium/titanium aluminium alloys and intermetallics is developed. The proposed technology is based on metallothermic reduction of titanium tetrachloride and utilizes a molten flux layer acting as a smart semipermeable liquid membrane. The intent is to improve the morfology of the titanium deposits in the Kroll process by depositing titanium in molten form with the aim to potentially produce titanium/titanium aluminium alloys more economically.

1. Introduction

The investigation is aimed at finding a better way of the production of metallic titanium and titanium-aluminium alloys from titanium tetrachloride using metal reducers.

At present, metallic titanium and titanium alloys are produced by vacuum arc remelting of sponge titanium (by the Kroll method) or of titanium powder (by the Hunter method), fig.1. [1].

The production of metallic titanium and its alloys is a multi-stage process. Let us use the Kroll method to illustrate it, [2,3].

- Production of a mass of sponge titanium from titanium tetrachloride by magnesium in a reactor of confined volume, where to liquid magnesium and liquid titanium tetrachloride are supplied. The reduction of titanium takes place in an inert environment along with recurring removal of magnesium chloride (as a reduction product).
- Cooling and evacuation of the reactor to remove the magnesium and magnesium chloride, aimed at the utmost purification of the produced sponge titanium.
- Extraction of the sponge titanium, partially welded onto the reactor wall, from the reactor.

- Fragmentation (crashing) and manual sorting of the sponge titanium fractions followed by their packing into sealed bags filled with an inert gas.
- Production of a titanium electrode sample for vacuum arc remelting by pressing the sorted fractions of the produced sponge titanium.
- Vacuum arc remelting of the electrode made from the sponge titanium to produce metallic titanium.
- Repeated vacuum arc remelting of the produced titanium ingot with alloying additions to obtain the required titanium alloy.

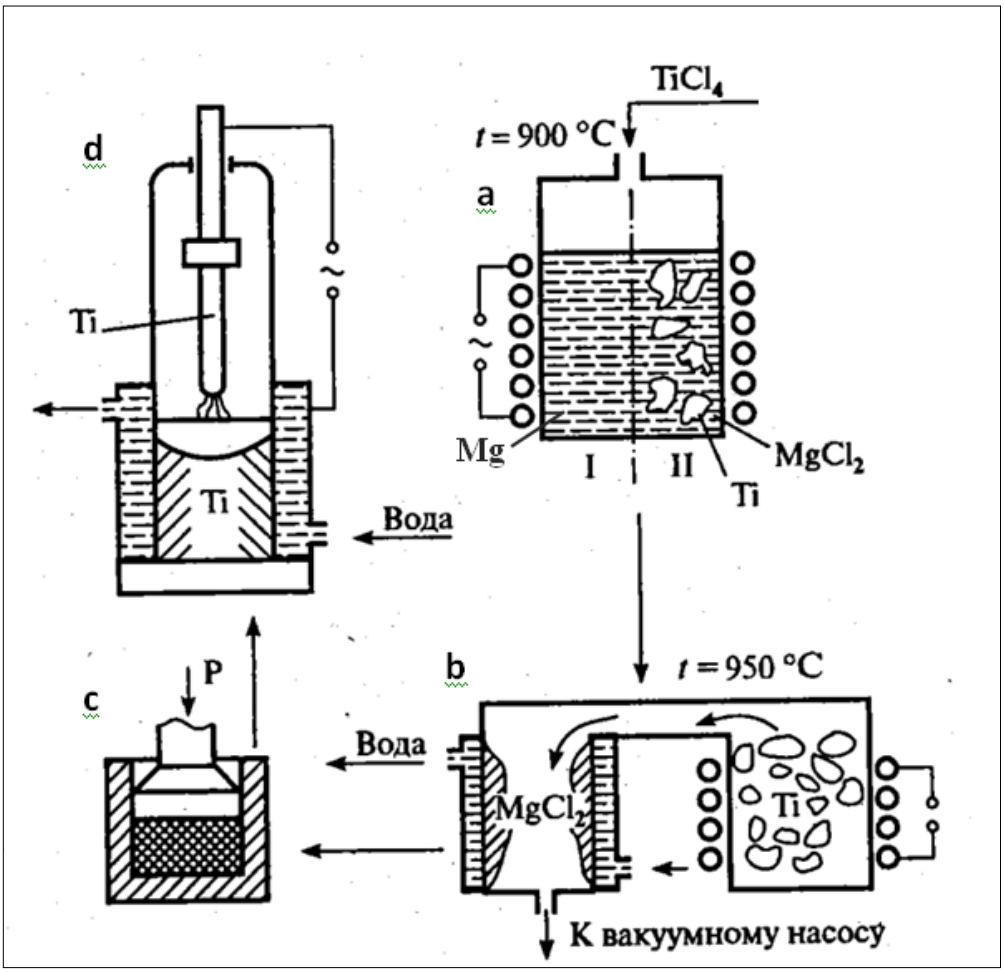

Fig. 1. Production of metallic titanium from sponge titanium by the Kroll method in the reactor: a) sponge titanium production by the Kroll method; b) sponge titanium purification; c) sponge titanium briquetting; d) electric arc remelting.

2. Presentation of the problem

In the course of the planned experiments, fig.2.we combine all the above-mentioned stages, simplifying in this way the technology of titanium and its alloys' production, in particular, of titanium-aluminium alloys. For this purpose, we intend to create such conditions in the reactor

which would contribute to the reduction of titanium from titanium tetrachloride by magnesium or by sodium as metal reducers, which implies creation of an inert environment in the reactor by evacuating the reactor, filling it with argon, and, when heating a solid or a liquid flux in the reactor, the reactor would be filled with the vapors of the melted flux. During the experiment, the flux in the reactor is heated by a power supply source to a temperature more that the titanium melting temperature, t = 1750°C – 1800 °C.

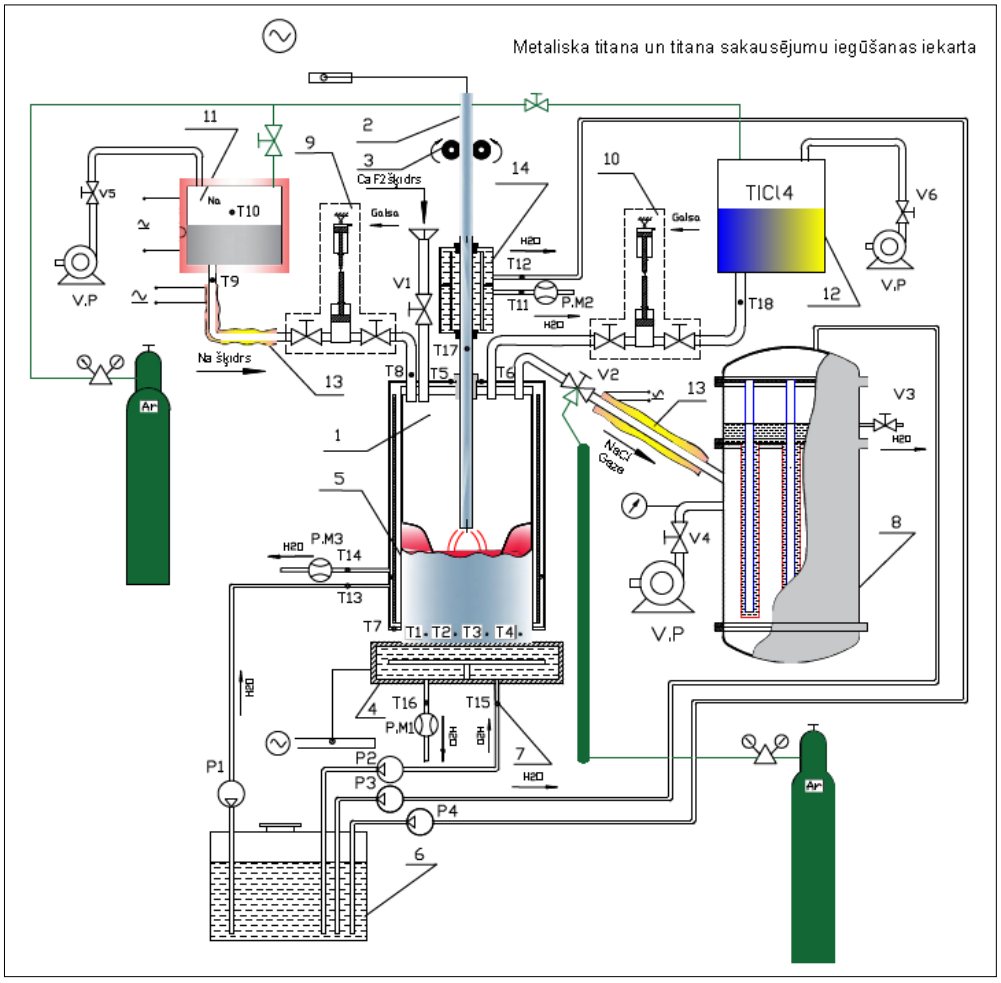

Fig. 2. Schematic presentation of the experiment: 1 – reactor, 2 – electrode, 3 – mechanism for controlling the electrode, 4 – metal cooling, 5 – alloying additions, 6 – bath (tank) with water, 7 – thermocouple T1-T18, 8 – condenser, 9 – sodium supply, 10 - TiCl4 supply, 11 – bath with liquid sodium, 12 – bath with liquid TiCl4, 13 – electric heater pipe, 14 - electrode cooling; P1-P4 – pumps; P.M1-P.M3 – flow meter.

When titanium tetrachloride and liquid magnesium or sodium (as metal-reducers) are supplied into the reactor by a dispenser, the reduction of titanium takes place in an environment containing a mixture of the flux vapors and argon, above the surface consisting of the liquid flux heated to the temperature t = 1750 – 1800 °C. All the reduced titanium as particles of sponge titanium when magnesium is used as a metal-reducer, or as powder when sodium is used as a

metal reducer, is precipitated onto the surface of the liquid flux bath heated to the temperature t = 1750 – 1800 °C, and a solid-to-liquid phase transition of the reduced titanium occurs. This transition takes place as on the surface of the liquid flux as when the titanium passes through the liquid flux.

Sponge titanium has the density 3.3 – 3.5 g/cm^3. The liquid flux used in the experiment must have a density lower than that of sponge titanium to provide the titanium pass through the liquid flux bath. During the planned investigations, fluxes will be selected not only by their density with regard to that of sponge titanium but also by the value of surface tension of the liquid flux as well as by other flux parameters which could affect the purity of the reduced titanium casted during electroslag remelting.

In the experiments, the parameters of the processes occurring in the reactor and determining the energy release during the reduction of titanium from titanium tetrachloride by magnesium or by sodium will be analyzed.

$$\mathbf{TiCl_{4(liquid)} + 2Mg_{(liquid)} = Ti_{(liquid)} + 2MgCl_{(liquid)}}$$

$$\mathbf{ДH_{reaction} = -393.9\ kJ/mol}$$

$$\mathbf{TiCl_{4(liquid)} + 4Na_{(liquid)} = Ti_{(liquid)} + 4NaCl_{(liquid)}}$$

$$\mathbf{ДH_{reaction} = -726.85\ kJ/mol}$$

The processes occurring in the reactor and in the condenser when the products of the titanium reduction by magnesium (magnesium chloride) or by sodium (sodium chloride) are removed from the reactor into the condenser will be also examined, in particular, the variation of the heat balance in the reactor at the removal of magnesium (or sodium) chlorides from it.

3. Conclusion

A basic scheme for investigation of the new method of the production titanium based on a combination of Kroll (Hunter) and electroslag melting techniques, is described.

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References.

[1] Tarasov A.V. Titanium Metallurgy. Moscow, Academkniga, 2003, 328 p., ill.

[2] Thomas M., Bacos M. P. Processing and characterization of TiAl-based alloys: towards an industrial,

Aerospace Lab. 2011. 3.pp. 1-11.

[3] Millls K.C., Keene B.J. Properties of molten CaF_2-based slags, International metals Reviews, 1981, 1, pp.21-69., Physicochemical