Electroslag process for better titanium deposition morphology

E. Platacis[1], I. Kaldre[1], E. Blumbergs[1], V. Serga[2]

[1]Institute of Physics, University of Latvia, Miera 32, Salaspils, LV-2169, Latvia
[2]Institute of Inorganic Chemistry, Riga Technical University, 3/7 P. Valdena, Riga, LV-1048, Latvia

Corresponding author: Imants.kaldre@lu.lv

Abstract
Most common process for titanium production nowadays is Kroll process. This process has several drawbacks. Process is cyclical, and titanium comes out in sponge like form. This means that process is long, reaction is uncontrollable and requires post-processing of titanium sponge, which is energy consuming. In this work we present the idea to use Kroll process combined with electroslag process to produce titanium in continuous, more efficient process. Main idea is to use heated reactor where the initial reaction products (titanium tetrachloride and magnesium) are injected in liquid and gaseous phases, and reaction takes place above liquid slag in gaseous phase. Slag layer ensures titanium separation from unreacted magnesium and magnesium chloride, and other reaction waste products. Titanium droplets filtrate through the slag and is separated from the other fractions. In this paper we test the feasibility of this idea by studying the electroslag remelting of a titanium electrode in a specially prepared laboratory reactor. Chemical analysis is done to measure the composition of reaction products.

Key words : Electroslag melting, Kroll process, Titanium

Introduction

An essential part of the Kroll process titanium production is post processing of the titanium sponge, which forms after the reaction [1]. Basic reaction is magnesium thermal reduction of titanium chloride.

$$TiCl_4\,(gas) + 2\,Mg\,(liquid/gas) = Ti\,(solid) + 2\,MgCl_2\,(liquid) \qquad (1)$$

This reaction is exothermal, the thermal dissipation for reaction (1) at 1100 K is equal to 686 kJ/mol [2]. This heat is enough to conduct the process without heat supply from the outside in industrial scale reactor. The lowest temperature limit of the reduction is restricted to the temperature of $MgCl_2$ melting (714°C) and the highest temperature limit is 975°C, when the temperature is higher, titanium actively interacts with iron, thus steel walls cannot be used. Practically, the process is conducted at 800-900°C in 1-3 m^3 large cylindrical reactors made of heat resistant steel [1-3]. At the same time, the optimal temperature for the reaction is 1200-1400°C [4]. At such a high temperature reaction takes place in a fully gaseous phase, and reaction products condenses on cooler surfaces. To ensure such temperature regime extra energy should be injected. One of the ways is insert additional heat via electric arch, which allows to increase temperature in the core of the reactor. Electric arch also improves the mixing of the reaction products and induces significant motion into the liquid slag. At temperature above 1200 ºC reaction at gas state takes place and titanium and reaction products forms as a powder at the surface of the liquid slag. Due to the density difference titanium droplets sinks through the slag, while $MgCl_2$ remains at the surface and can be periodically drained from the reactor. Thus, in this case slag layer acts as a smart membrane separating the reaction products.

In this work preliminary experimental results acquired by small laboratory scale experimental setup is presented and numerical and analytical results showing the potential of this technology is given. Basic idea is to use high temperature reactor where titanium tetrachloride is reduced with magnesium, while liquid slag layer is placed bellow reaction zone as shown in principal scheme in Fig.1. Reactor walls are water cooled stainless steel and solid slag layer is forming on the walls thus protecting them from contact with titanium at high temperature. As solid slag is a poor thermal conductor, this layer also serves as thermal insulation limiting heat flux through the walls. For the elaboration of the technical parameters of the process in the first experiments NaF was used as a slag, but it is planned to investigate the performance and compare several different slags (CaF_2, NaCl and others).

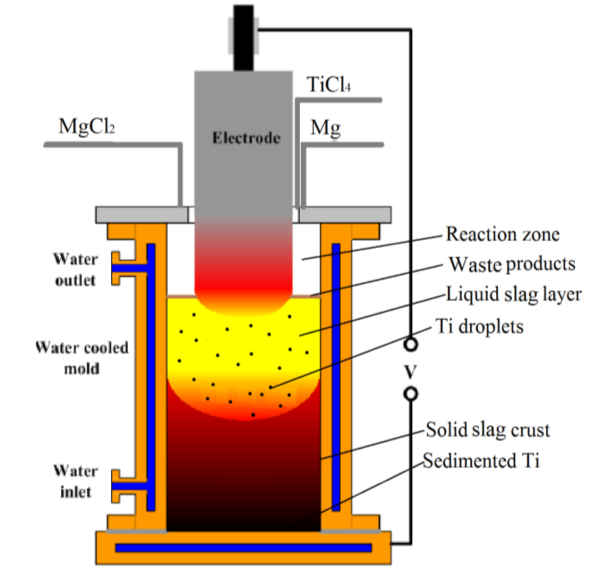

Fig. 1. Scheme of the combined Kroll and electroslag processes

Results and discussion

Small scale experimental facility has been designed and built to test the reaction kinetics at elevated temperature and to test the validity of the idea to use slag mixture as semi-transparent membrane for reaction product separation. First experiments are done using titanium electrode, which partly melts. The aim of these experiments is to test the hypothesis about titanium droplet sinking through the slag layer and to measure the morphology and chemical composition of sedimented products at the bottom. Inner diameter of the reactor is 60 mm. Reactor is filled with liquid slag at height of 120 mm. Titanium electrode of 14 mm in diameter is immersed into the slag. Argon was fed to the chamber at a rate of 10 l/min, maintaining small overpressure. Overall scheme of the experimental setup is given in Fig. 2(a).

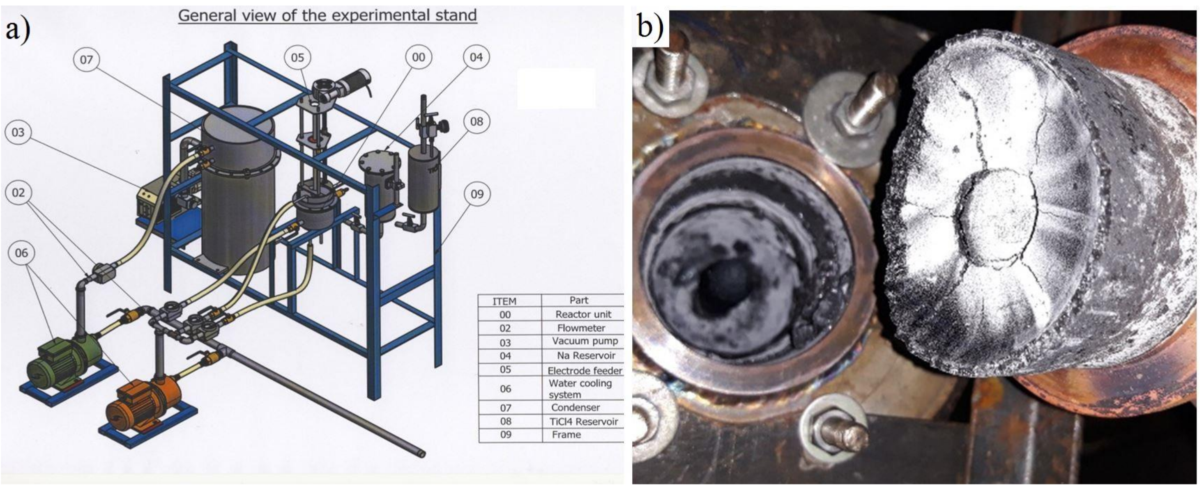

Fig. 2. a) Scheme of the experimental setup; b) Titanium reactor and solidified content after reaction

Solidified NaF slag after the experiment is shown in Fig.2(b). On the right side is solid NaF, and on the left side Ti electrode and inner surface of the reactor with a slag crust is visible. Approximately 10 kW (20 V, 500 A) of electric power is applied during experiment. Titanium electrode starts to melt in this process and titanium sinks through the slag layer. Titanium droplets at the bottom were analyzed by X-ray diffractometry, and results show that droplets consist of 80 % titanium and 20 % of titanium oxide TiO. According to the XRD analysis (Fig. 3), material contains a titanium as the main phase of the titanium and TiO as an impurity [5]. Elemental analysis of slag showed the presence of small amounts of titanium in it (0.06-0.50 wt.%). This may be explained by the fact that small droplets sink slowly and was trapped in slag during solidification after the heating was turned off.

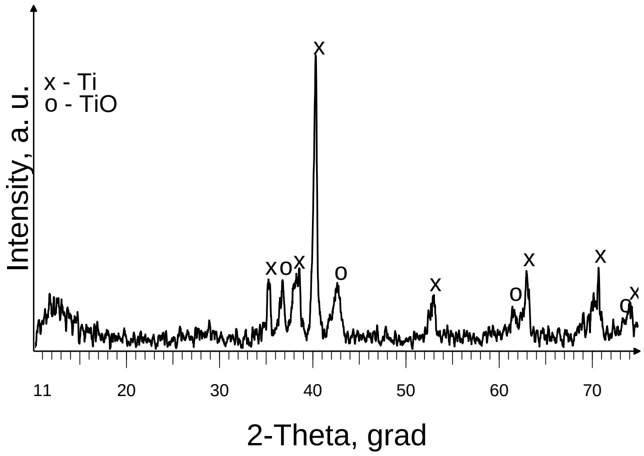

Fig. 3. XRD pattern of the titanium droplets

Slag layer may significantly change the morphology of the titanium deposition as titanium droplets are filtering through it rather than solidified directly in the reactor. It is shown that this process can be done in small semi-continuous reactor by electric arc heating. Numerical simulation demonstrates that reaction products can be heated up to 1500 °C by electric arch (Fig.4(b,c)), while reactor walls are protected by thin solid crust of the slag material. Numerical models to describe thermal regime, fluid flow and electromagnetic processes in reactor are developed. Axisymmetric Comsol 5.0 numerical model with 8000 cells was developed. Density of the slag is described by following linear function: ρ[kg/m^3]=3070-0.39·T[°C]. Thermal conductivity of slag is 1 W/m·K, electric conductivity 150 sim/m, viscosity 0.006 Pa·s [6].

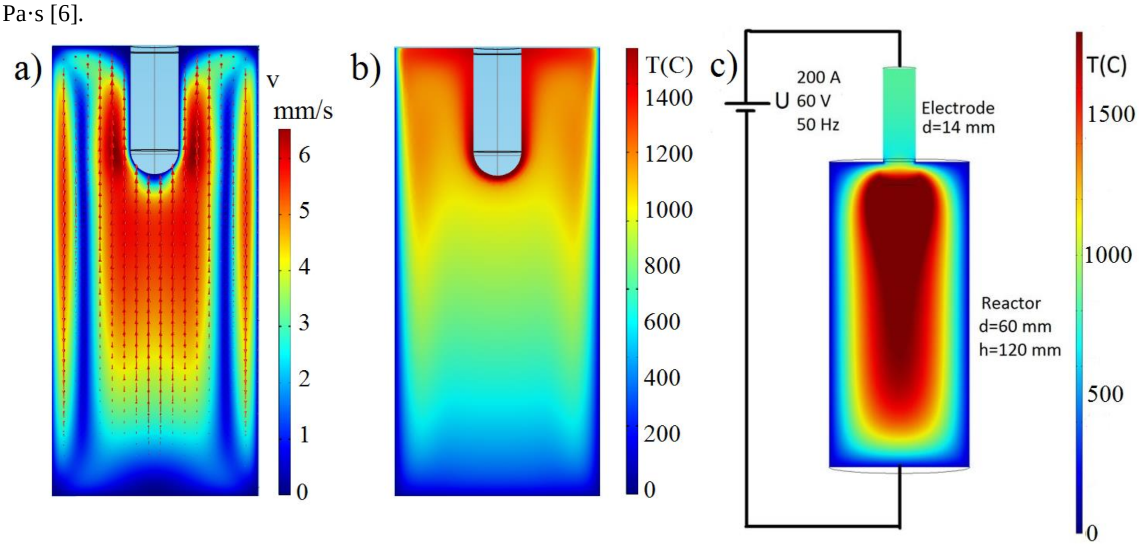

Fig. 4. a) Numerically calculated velocity distribution of the liquid slag; b) Temperature distribution in reactor chamber; c) temperature distribution if the slag is solid

Numerical models show that significant natural convection appears in the crucible if slag is fully liquid. Convective flow of 5 mm/s completely change the temperature distribution in the reactor as shown in Fig. 4(a).

Numerical simulations show that in case of stationary volume high temperature can be reached near the electrode as shown in Fig. 4(c). Still the precise location of solidification interface is difficult to locate, but solid crust layer is estimated to be 3-5 mm thick. Natural convection of the slag significantly affects the temperature distribution in reactor. Nevertheless, numerical model confirms that even with convection expected temperature is reached near the electrode. One of the problems is that data on the properties of the slag is fragmentary and they may vary significantly depending on temperature, impurities and other factors.

Conclusions

It has been shown that Kroll process can be replicated in small scale reactor with additional electric arch heating. Series of experiments has been done, showing that reactions take place. First experiments with liquid slag layer shows that titanium droplets sink to the bottom of the reactor through the liquid slag layer. Effective removal of the reaction waste products remains one of the experimental obstacles, because slag layer at the surface significantly decreases the process efficiency. Numerical simulations of temperature distribution and liquid slag motion has been done. It is shown that temperature distribution is largely affected by liquid slag natural convection which arises due to localized heat distribution near the electrode. Numerical models confirm that we can expect that reactor walls are protected by solid slag layer. The obtained data demonstrate the possibility of combining the Kroll process and the electroslag process with the installation described in this paper. Within current research project it is planned to developed larger experimental setup to test the whole process in laboratory scale.

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