

## DEVELOPING A NEW CONTINUOUS PROCESS FOR MAKING TITANIUM

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### ABSTRACT

R. Winand invented a new process to prepare titanium ingot in one step from sodium and titanium tetrachloride. Making use of the two reagents in the gaseous phase and recovering titanium as a liquid on top of a continuous casting mould, sodium chloride is also gaseous, so that titanium is the only condensed material. This process has the following features : it is continuous; the number of intermediate stages are dramatically decreased compared to the Kroll or the Hunter processes; the manpower and the metal inventory are much lower, the energy consumption is decreased while only small amounts of reagents are involved in the reaction at any time so that hazard problems are highly reduced, the metal recovered as an ingot is very pure while the metal not included in the ingot can be sold as a powder, it could also be used to prepare titanium alloys in ingots, or powders of pure titanium or of alloyed titanium including intermetallic compounds. The research started ten years ago at laboratory scale. Since 1987, a pilot capable of 25 kg titanium per hour is operated in the hall for testing prototypes of the Centre de Recherches Industrielles of the Université Libre de Bruxelles. So far, sodium and titanium tetrachloride handling and gas production are under control, giving stable and reproducible constant gas flows. Sodium chloride condensation is also satisfactory. The reaction occurs at high speed and gives the expected high temperatures. However, as it was thought that the heat of reaction is high enough to heat up the reaction chamber, no preheating system was provided. After trying a number of injectors, and also after mathematical modelling, it was shown that preheating is absolutely necessary, otherwise the transient lasts long enough for the reaction chamber to be clogged with partially molten reaction products. Further research including electric resistance preheating showed this method to be inefficient. Despite of that, reactions lasting for two hours were performed, but titanium was recovered as conglomerates of particles instead of a molten pool. Future experiments should make use of other preheating systems.

### INTRODUCTION

Owing to its exceptional properties and to the availability of suitable ores, titanium should undergo a wide market expansion. This was not the case so far because the price of the metal is still too high to make it competitive against other materials like for instance stainless steel. Accordingly, except in countries where an industrial strategy for titanium development exists, the uses of this metal and its alloys are restricted mainly to aeronautics, aerospace and chemical industry applications. In fact, there is a need for a new industrial process for making titanium, able to reduce markedly the base metal cost. The Kroll and Hunter processes used today are based on the discontinuous metallothermic reduction of titanium tetrachloride either in one step by magnesium or in two steps by sodium. Despite improvements described in literature [1-3], they involve many operations before getting an ingot suitable for further processing. Attempts to develop alternative processes were up to now largely unsuccessful.

to (%) 0.02 in iodide titanium, 0.04 - in titanium sponge  $\text{Ti} -90$  and 0.06 - in titanium sponge  $\text{Ti} -120$ .

The oxygen content in the ESR metal in its stable level (start zone being excluded) remains equal to its content in the initial metal. The content of harmful impurities by the height of the ESR ingot of 60 mm in dia. and 150 mm in height remelted from titanium sponge  $\text{Ti} -120$  is presented in the table:

Sites of sampling	Fraction of total mass (%)			
	H	C	N	O
Top	0.003	0.01	0.005	0.06
Middle	0.004	0.01	0.005	0.06
Bottom	0.005	0.01	0.008	0.08

#### References

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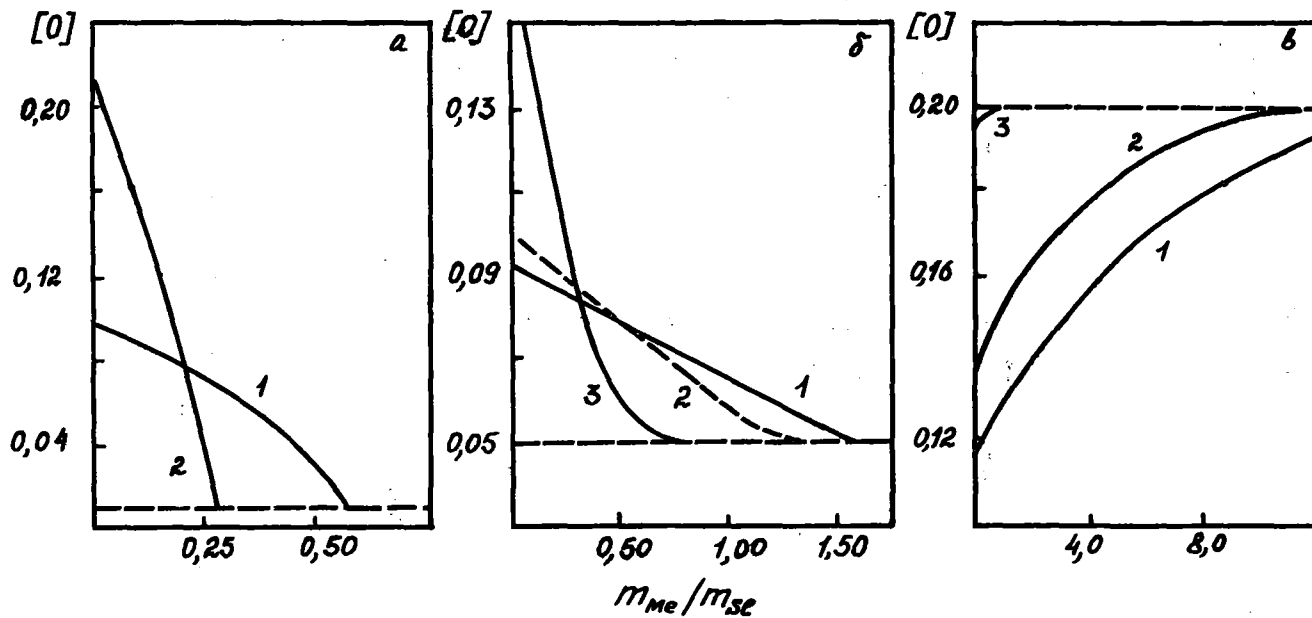


Figure 2. Dependence of the oxygen content in titanium on the relative weight of the melted metal with the oxygen content in the electrode, %: a - 0.01, - 0.05, - 0.2 (1-2, 2-1, 3-1  $10^{-5}$  % (Ga) ).

med on microcomputer by a special program which realizes the described algorithm.

Remelting of titanium with oxygen content 0.01; 0.05; 0.2% is considered. The flux consists of a pure calcium fluoride; the content of calcium oxide in it is assumed as 0.1% which corresponds to the content of this admixture in the most pure flux. The content of calcium in the flux varies from 2.0 to 0.000001% (small values approaching zero). The results of the calculations are presented in Fig. 2.

Proceeding from the above calculations it is possible to conclude as follows: under electroslag remelting it is not possible to obtain the oxygen content in titanium lower than in the consumable electrode. In the case when the initial content of oxygen in the consumable electrodes is small (Fig. 2 a, b) the content of oxygen in the metal at the beginning of heat sharply increases, especially when using flux without metallic calcium, then the oxygen content in the ingot falls to the values in the consumable electrodes. Apparently, it is attributed to reduction of the calcium oxide by titanium at the initial period and dissolution of oxygen in titanium. If the flux contains metallic calcium such processes proceed less intensive and restoration of the initial oxygen content is not so fast since in this case the reduction reaction of calcium oxide is retarded.

When the oxygen content in the consumable electrode is increased (Fig. 2 a) then in absence of metallic calcium in the flux the content of oxygen in the ingot remains initial.

If at the initial period of heat the metallic calcium is introduced into the flux then the oxygen content becomes lower and becomes equal to the content of oxygen in the consumable electrode. Apparently, it is connected with the following fact - when the heat starts calcium interacts with titanium oxygen and the more is the flux saturated with the product of the reaction (calcium oxide) the more it hampers the reaction.

Electroslag remelting of titanium has been performed in the mould of 60-120 mm in dia., ingots of 100-250 mm in height have been produced. Electrodes have been melted from iodide titanium or produced by compaction of the titanium sponge (TF - 90 and TF-120 grades).

Oxygen content in the consumable electrodes has amounted

siderable then the expression (I3) may be simplified:

$$K_2' = X_{(CaO)} / (P_{Ca} [O]) \quad (I4)$$

where  $X_{(CaO)}$  - fraction of total mass of CaO in slag;  $P_{Ca}$  - pressure of calcium vapour, MPa.

Proceeding from the expressions (I2) and (I4) write as

$$\exp(0,50717 - 0,44097/[O]) = X_{(CaO)} / (P_{Ca} [O]) \quad (I5)$$

$$P_{Ca} = a_{Ca} P_0^{Ca} \quad (I6)$$

where  $a_{Ca}$  - calcium activity in the melt Ca-CaF<sub>2</sub>;

$P_0^{Ca} = 53,651 - 12826,75/T + 0,002T - 14,485 \lg T$  - vapour pressure over pure calcium, MPa.

Calcium activity in the slag is determined by the procedure presented in the work [5].

A portion (drop) of titanium of the weight  $m_{Me}$  (kg) containing  $O_{initial}$  of oxygen, and slag of the weight  $m_s$  (kg) containing  $(Ca)_{initial}$ ,  $(CaO)_{initial}$ , CaF<sub>2</sub> - the base) interact under electroslag remelting. Transition of a definite quantity of oxygen ( $\Delta [O]$  %) from the metal drop into slag is described as follows:

$$[O] = [O]_{initial} - \Delta [O] \quad (I7)$$

$$(Ca) = (Ca)_{initial} - \Delta [O] (m_{Me}/m_s) (\mu_{Ca} / \mu_o) \quad (I8)$$

$$(CaO) = (CaO)_{initial} + \Delta [O] (m_{Me}/m_s) (\mu_{CaO} / \mu_o) \quad (I9)$$

where  $\mu_{Ca}$ ,  $\mu_{CaO}$ ,  $\mu_o$  - molecular mass of calcium, calcium oxide and oxygen, respectively.

Solving the equation (I5) by the iteration method with regard for the expressions (I7)-(I9) find equilibrium values  $[O]_p$ ,  $(CaO)_p$ ,  $(Ca)_p$ , a portion of metal with oxygen concentration  $[O]_p$  solidifies and does not participate in the reactions any more. A new portion of metal with  $[O]_{initial}$  is introduced into the slag of composition  $(Ca)_p$ ,  $(CaO)_p$  and new equilibrium concentrations are considered. So, it is possible to determine the oxygen content in the ingot depending on the weight of the remelted metal. Calculations were perfor-

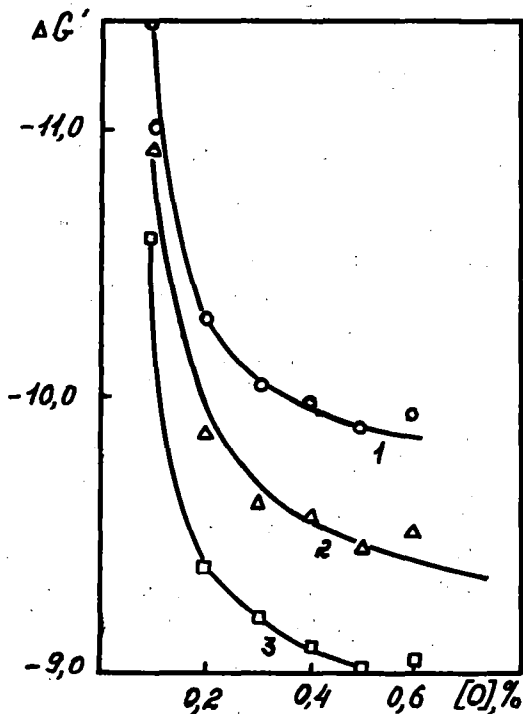


Figure I. Dependence of partial mole Gibbs energy ( $\Delta G^I$ , kcal/mol) of the reaction of oxygen dissolution in titanium on the oxygen concentration in titanium at the temperature, K: 1 - 1973, 2 - 2073, 3 - 2273.

With regard for the dependence (6) and the value  $\Delta G_3 = -93050$  cal/mol [7] for  $T = 2073$  derive:

$$\Delta G_7^I = -2089,072 + 1629,258 / [O] \quad (II)$$

$$K_7^I = \exp(0,50717 - 0,444097 / [O]) \quad (I2)$$

For the reaction (7) write as

$$K_7^I = a_{(CaO)} / (P_{Ca} [O]) \quad (I3)$$

Since the content of calcium oxide in the slag is incon-

pressure of oxygen in the gas phase, MPa;  $\Delta G$  - variation of the partial mole free energy of oxygen in titanium, kcal/mol.

Results of the experimental determination of  $\Delta G$  in titanium-oxygen alloys presented in the work [3] have shown a dependence of  $\Delta G$  on the oxygen content in titanium. It is connected with the fact that oxygen solution in titanium even in small concentration deviates considerably from the Henry law.

Since there is no reliable information on the values of the coefficient of oxygen activity in titanium let us introduce the notion of the effective constant of the reaction (I):

$$K'_P = K_P / \gamma_0 = [O] / P_{O_2}^{1/2} \quad (4)$$

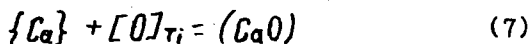
then

$$\Delta G' = -RT \ln K'_P \quad (5)$$

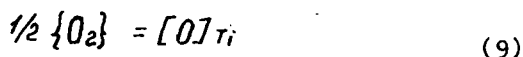
A dependence presented in Fig. I is obtained on the basis of the experimental data from work [3]. Hyperbola approximation of table values at 2073 K is introduced for determination of the analytical dependence:

$$\Delta G' = -90960,928 - 1829,258 / [O] \quad (6)$$

Interaction of oxygen in titanium with calcium dissolved in calcium fluoride is presented as a reaction:



which may be obtained by the combination of two following reactions:



Then

$$\Delta G_7 = \Delta G_8 - \Delta G_9 \quad (10)$$

Development of engineering and extension of the spheres of scientific research depend more and more on the use of pure metals and alloys. The existing industrial methods for their production are based on vacuum remelting processes (vacuum arc and electron-beam remelting) which in a number of cases do not provide a necessary purity of metals. At the same time such high-effective methods as iodide refining, distillation and others are characterized by low productivity and high cost [1, 2].

Electroslag remelting (ESR) in the atmosphere of inert gas under highly deoxidized fluxes is an alternative to vacuum remelting. Study of ESR under active fluxes including calcium-containing ones has shown wide potentialities of this technological variant for production of top-quality ingots of reactive metals.

Metal-slag fluxes, particularly Ca-CaF<sub>2</sub> systems, provide effective refining of the remelted metals from impurities that possess a considerable thermodynamic affinity to the applied alkali-earth metals (oxygen, nitrogen, phosphorus, sulphur). Besides, intensive evaporation of metallic calcium from slag in the course of melting permits achieving rather low partial pressures of harmful gases (oxygen, nitrogen, hydrogen) in the melting cavity. For example, equilibrium partial oxygen pressure at the temperature of remelting is 10<sup>-20</sup> - 10<sup>-25</sup> atm. The latter circumstance allows a contamination-free remelting of titanium possessing high thermodynamic affinity to the above gases.

An attempt is made to evaluate behaviour of oxygen during ESR of titanium under flux of the metallic calcium - calcium fluoride system.

Dissolution of gaseous oxygen in titanium is described by the equations:

$$\frac{1}{2} \{O_2\} = [O]_{Ti} \quad (1)$$

$$K_P = \gamma_o [O] / P_{O_2}^{1/2} \quad (2)$$

$$\Delta G = -RT \ln K_P \quad (3)$$

where  $\gamma_o$  - coefficient of the oxygen activity;  $[O]$  - fraction of total mass of oxygen in titanium, %;  $P_{O_2}$  - partial