

THE PRODUCING HYDRIDES IN TITANIC POWDERS UNDER DIFFERENT WAY OF PRODUCTION

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The saturating by hydrogen always accompanies process of reception of titanic sponge, powders, and also alloys. The non-ferrous metallurgy delivers basic weight of metal with the contents of hydrogen less allowable concentration, at which the hydrogen fragility is possible. However, in the process of manufacturing of powders and at technological operations during manufacturing products the increase of concentration of hydrogen up to level resulting in creation of titanium hydrides is possible [1]. During production of powders or manufacturing of products in such cases the development of hydrogen fragility is possible. Therefore, the struggle with the saturating by hydrogen is one of major problems in production of titanic powder products used in a space and aircrafts industry, mechanical engineering, rocket production.

On the other hand, hydrogenation of titanium is widely used in industry, and the area of application of titanium hydride extends, also ways of hydrogenation are being improved. Hydride of titanium is applied in nuclear engineering, in reactors of nuclear engines for the space equipment, electronics, cermet manufacturing, power engineering. Hydride of titanium is an effective tool for biological protection against neutrons and rigid γ -rays. Recently process of hydrogenation was used as an effective way to crisp the titanium wastes of materials to make them finer [2]. The growing interest in modern engineering to problems of hydrogenation in titanic powders leads to the necessity of careful study of this process.

In this connection an urgent problem in production of titanium sponge and powders is the all-round regular study of the process of hydrogenation in powders of titanium, obtained in different ways.

The saturating by hydrogen of powders can occur at all stages of production, and in particular at the stage of their hydrometallurgical processing, because particles, which adjoin with electrolyte and with a water solution of a hydrochloric acid cooperate with atoms of hydrogen, chlorine, oxygen, hydroxide groups.

There is practically no free hydrogen in the environmental atmosphere. The main source of the saturating by hydrogen in the process of producting of titanic powders is electrolyte, melt, water

solutions of a hydrochloric acid at lixiviation. While interacting with titanium, hydroxide group (HE) is decomposed into oxygen and hydrogen, i.e. on the surface of particles there will be simultaneously both atoms of hydrogen and atoms of oxygen, which begin to penetrate in the depths of metal.

Titanic powders received by different ways have structure α -Ti, having two types of pores: octahedral and tetrahedral with the size of radius of an interstice equal to 0,62 nm and 0,34 nm accordingly. The speed of diffusion of atoms of implementation in titanium varies and also depends on the size of their radiuses, which is illustrated in Tab. 1. The atoms of these gases settle down in octahedral pores of a firm solution, instead of in tetrahedral, only because they are larger. Octahedral pores less rigid than tetrahedral and easily increased in sizes in the direction of the least diagonal octahedron [3]. The hydrogen, being in such emptiness, has large freedom of fluctuations of atoms, that increases energy of the system. For this reason the solubility of hydrogen in α -phase is small.

Table 1. Speed of diffusion of atoms of implementation in titanium

The name of an element	Speed of diffusion $\cdot 10^{-15}$, m/s	The size of nuclear radius $\cdot 10^{-10}$, m
O	1,6	0,68
N	1,2	0,74
H	2,0	0,41
Cl	0,9	0,99

On the other hand in VCK lattice β -modifications of titanium of emptiness with radius 0,44 nm almost precisely correspond to nuclear radius of hydrogen 0,41 nm and free fluctuations of atoms between knots do not occur. Therefore the hydrogen is well dissolved in β -phase up to (2 %), stabilising it [3].

As it is shown in Tab. 1, the hydrogen has the highest speed of diffusion, the size of radius of its atom is $0,41 \cdot 10^{-10}$ m, and the size of octahedral pore in α -Ti is $0,62 \cdot 10^{-10}$ m, i.e is 34 % less than the size of octahedral pore of a crystal lattice of

titanium. Moving along octahedral pores, the hydrogen freely and quickly goes in the depth of a particle.

At the same time, the oxygen has high enough speed of diffusion $1,6 \cdot 10^{-15}$ m/s, but the size of its atom radius is 10 % larger than the size of octahedral pore α -Ti. Therefore, already at room temperature the atom of the oxygen which has got in octahedral pore, stretches it but can not leave it. Thus, a monolayer of oxide film is formed on a surface of a particle of a powder.

Since titanium as the chemically active element can change valence from -2 up to +4 during lixiviation on the surface of a particle there can be more than one kind of compounds of titanium with oxygen.

In Tab. 2 the data on entropy are presented, as well as data on enthalpy of compounds of titanium with a solution of an acid on a surface of a particle.

Table 2. Thermodynamic properties of connections of titanium with oxygen, nitrogen, hydrogen

Compound	Entropy, Dg/mol·deg	Enthalpy, κDg/mol	Fusion temperature, °C	Density, kg/m ³
Ti ₂ O	–	177,9	1540	4950
TiO	34,8	608-518,7	1750	4930
Ti ₂ O ₃	78,7	1627-1519	1900	4550
Ti ₃ O ₅	129,4	2457	2177	4570
TiO ₂	50,2	913,4-944	1850	4260
TiN	30,1	336	2950	4220
TiH ₂	62,6	29-31	650	4150

From Tab. 2 it is visible, that titanium hydride has low enthalpy equal 29-31 κDg/mol and high entropy for formation and creation of the ordered system TiH₂. These are the lowest thermodynamic parameters in creation of not metal connections of titanium among oxides, nitrides and hydrides. X-rays investigations of powders of various firmness after corrosion tests in solutions of a hydrochloric acid of various concentration has established that during first hours oxide Ti₂O is formed. Its enthalpy is 177,9 κDg/mol. With increase of time of endurance in a solution of a hydrochloric acid the valence of titanium varies from -2 up to +4 and thus enthalpy grows up to 944 κDg/mol (TiO₂).

This is confirmed by investigation the fulfilled solutions, where valence of ions of titanium after an output in a solution was determined. Therefore, for the following portions of hydrogen to penetrate deep into particle, it is necessary to overcome a monolayer of titanium oxide Ti₂O, settled down on a surface of particles of titanic powders. Oxide film drastically slowed down the diffusion of hydrogen deep into the metal. Besides the oxygen having high speed of diffusion, also trying to diffuse with a surface deep into particles, thus forming alpha layer enriched by oxygen.

As it was established by metallographic investigations, the top alpha layer does not contain hydrides, they occur in structure of metal on some distance from a surface. Hydride needles are placed in all volume of a particle with an angle 60 and 120 degrees to each other. Therefore, the content of oxygen influences the solubility of hydrogen in powders.

As the computer processing of the statistical data has shown, there is a direct correlating interrelation between hydrogen and oxygen. The content of hydrogen grows with increase of the contents of impurity in powders and with change of a way of production.

By results of the carried out researches it is possible to conclude:

- the properties of titanic powders essentially depend on the contents of gas impurity in powders;
- there is an interrelation between the contents of hydrogen and oxygen;
- structure, mechanism of growth, morphology of hydride creations depend on a way of manufacture of titanic powders.

References

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