INFLUENCE OF MILD AGGRESSIVE ENVIRONMENTS ON FORMATION OF HYDRIDES IN TITANIUM POWDERS

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Hydrogen interacts practically with all metals forming simple chemical compounds, hydrides, which recently find ever-wider applications in different industries. Titanium hydrides are getters in electronics or moderators and deflectors in nuclear and space technologies. Association of hydrogen with a metal involves a number of specific processes: braking bonds in the molecule of hydrogen with formation of atoms and ions, chemical adsorption, penetration of hydrogen inside the metal, filling in the octahedron-shaped pores, further bonding with ions of the metal and forming the hydride layer. For corroboration of interaction of titanium with hydrogen in solutions of hydrochloric acid the following researches have been conducted. Certain portions of titanium powder were placed into solutions hydrochloric acid of different concentration for exposing during 5, 10, 25, 50, 100, 500, 1000 hours [1]. After the time of exposure expired samples were tested with X-ray radiography (determination of phase composition, parameters of the crystal lattice, intensity of lines of ά-titanium, dimensions of blocks), metallography (study of the microstructure on the surface and in cross-sections of particles of the powder) and the used solutions were analyzed.

Since titanium is an active chemical element due to lack of electrons on 4s- and 3d-sublevels of N- и M-levels, in interaction with hydrochloric acid atoms of titanium become excited. An excited atom of titanium begins to give up electrons into the solution of the acid becoming a positively charged ion. Excited atoms of chlorine, hydrogen and oxygen converted into negatively charged ions bond with positively charged atoms of titanium depending on the speed of diffusion of gases.

Hydrogen, having high speed of diffusion, will be the first to reach the surface of the particles of the titanium powder. An ion of hydrogen and an ion of the metal form a common electron pair with a covalent bond, which belongs to both elements. In parallel, atoms of hydrogen will be the first to accept uncoupled atoms of titanium, since they, earlier than other gases, fill in the close to the nucleus electron level due to high ionizing potential. Other free atoms of hydrogen penetrate in the depth of the metal and fill in the octahedron-shaped pores of titanium.

The strongest bonds titanium may have with oxygen and hydrogen because they form completed 1s- and 2p-levels close to the nucleus. Hydrogen and oxygen complete their levels by joining one and two electrons from titanium respectively.

Research of the parameters of the lattice of titanium powders of different hardness after exposure to solutions of the acid showed that during the early hours the strongest changes of parameters of the lattice are observed in the powders treated in condensed solutions of the acid.

It is known from sources [2] that ά-Ti has the strongest reflection of X-rays (101), which corresponds to the angle of reflection of 40,2°. A strong interference line of the titanium hydride (200) is obtained at the reflection angle of X-rays of 40,23°. Interference lines reflected from planes (101) of ά-Ti and (200) of TiH have practically same inter-band intervals and rays reflected under the same angle overlap. Angles of reflection of ά-Ti and titanium hydride practically coincide, and it is difficult to distinguish which phase it is. Other lines are needed for this, closely located as well as significant. For ά-Ti a closely located and medium-significant is the interference line of plane (002), corresponding to the reflection angle of 38,5°. Titanium hydride, reflecting an X-ray from plane (100) has an interference line of medium significance at 35,19°. Simultaneously dimensions of the intensity of the lines of all phases are measured (Fig. 1).

As one can see in Fig. 1, the intensity of the interference line belonging simultaneously to two phases, with the growth of concentration of the acid decreases in 1000 hours by 3.1 times. The common line on the X-ray picture of a titanium powder kept in 30 % solution of hydrochloric acid has smaller size than the same line of the powder kept in 37 % solution. This due to its splitting into two other lines belonging to ά-Ti and to TiH_2. It was established that line (002) ά-Ti also changes non-uniformly. The magnitude of the peak of the line in comparison with the initial state decreases 3 times. In a 10 % solution of HCl the split is observed, and in 15 % solution appearance of plane (004) belonging to TiO phase was found.

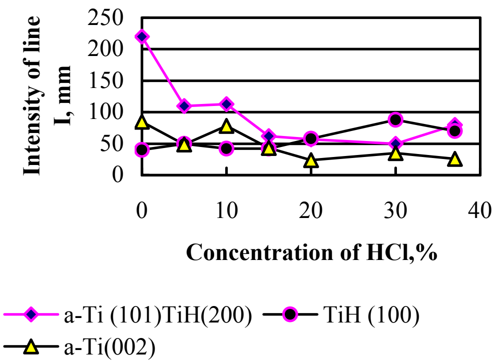


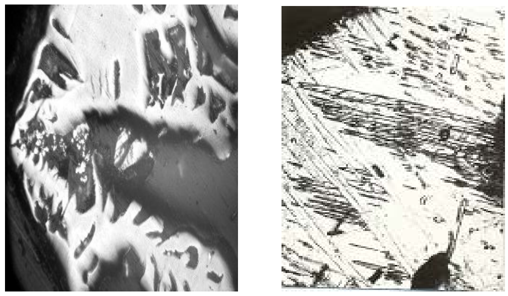
Fig. 1. Change of intensity of reflection lines in titanium powders depending on concentration of the hydrochloric acid.

The sizes of the interference lines of TiH (100) of titanium powders held in solutions of titanium powders doubled while the concentration of the acid increased. It has been proven that the line of titanium hydride in 5, 15, 20 % solutions of HCl splits, which explains additional aberration of the crystal lattice of titanium and appearance of a new plane belonging to TiH.

The transition of ions of titanium into the solution of hydrochloric acid has been confirmed by analyses of chemical and electronic paramagnetic resonance. Titanium in solutions of hydrochloric acid showed valence 3, that is, it gave three electrons into the solution for forming electron pairs with hydrogen and oxygen.

As chemical analysis has shown, after 1000 hours of exposure to the acid solution, non-metallic compounds formed in the solution, which precipitated. This has been confirmed by determining the intensity of the lines with the use of the method of electron paramagnetic resonance as well as by radiography researches of the parameters of the crystal lattice and determination of the phase composition of the powder.

The microstructure of the particles of the titanium powder also was changing: while in the initial particles the structure is represented by ά-titanium (Fig. 2a), then already after 100-hour exposure in the cross-sections of the particles hydride needles were found positioned at angles of 120° and 60°. After 1000 hours of exposure to the solution of hydrochloric acid the microstructure in the cross-sections of the particles of the powder is represented by ά-titanium and large hydride needles piercing the particle from one boundary to the other (Fig. 2b).



a) b)

Fig. 2. Microstructure of particles of titanium powder, ×300: a) initial; b) after 1000 h exposure to a solution of hydrochloric acid.

Conclusions

Thus, in this work it has been shown that conducted researches in weak aggressive environments change both the environment and the titanium powder. It has been established that trivalent titanium goes into the solution of hydrochloric acid, while particles of titanium powder get saturated with atoms of hydrogen and oxygen. Saturation of the powder occurs uneavenly and depends both on the time of exposure and the concentation of the acid. The X-ray radiography researches have shown and proved that atoms of hydrogen penetrating into the crystal lattice distort ά-Ti in such a way that intensity of the line reflected by plane (002) decreases, while the intensity of the line reflected by plane (100) of the titanium hydride.

References

1.Babenko E.P., Interactions of Hydrogen with Interstitial Impurities in Titanium Powders / E.P. Babenko, O. M. Shapovalova / VII International Conference Hydrogen Materials Science and Chemistry of Carbon Nanomaterials. – Sudak, 2007. – P. 95-97.

2. Titanium Alloys. Metallography of Titanium Alloys. Glazunov S et al. M.:Metallurgiya, 1980. – 464p. (in Russian).