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Titanium — Key to Ocean Depth

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Titanium and its alloys find application in many industries due to high specific strength and corrosion resistance in many aggressive medias. Especially brightly specified properties of titanium are appeared at use in structures of sea and offshore application in which rather high cost of titanium is compensated by weight reduction of structures and increase in their operational resource. In the report are analyzed the basic tendencies of development and also expansion of the sea application and offshore industry, the optimal chemical composition of titanium alloys are considered. Are considered problems of application of titanium for the equipment used for producing of hydrocarbons on the great depths and also application of titanium for deep-water devices. It is shown that application of titanium allows to solve problems of ultra-deep boring not only due to weight reduction of the equipment but also high resistance in such corrosion medias as oil, gas, stratal water, drilling mud and others. Are analyzed advantages of application of the titanium compared with other structural materials for the deep-water devices intended for a various kind of underwater operations on the big depths such as saving, sea geological prospecting, construction, repair of underwater structures and others. Taking into account that with an increase in the permissible submersion depth of devices the requirements of the accuracy of geometrical forms raise, technological questions of their manufacturing are considered in the report.

Keyword: titanium (Ti), hydrocarbons, deep-water devices, corrosion medias

1. Introduction

The marine and offshore structures for which common operating environment is sea water should be manufactured from material offering high mechanical strength and resistance to corrosion in this medium as well as high specific strength.
The material that most efficiently meets these requirements is titanium. The main consumer of titanium up till now has been the airspace industry and yet it is progressively rivaled by other industries, such as shipbuilding and offshore in particular, due to their increasing importance.
The increasing scope of uses of titanium in shipbuilding and offshore industries is reflected by the number of papers on this matter published in proceedings of International conferences on titanium. Thus presented on the 3-d International conference in 1976 was only one paper on this subject, on the 9th conference in 1999, were 12, on the 10th in 2003, there were 9 papers. It should be noted that because the marine application of titanium in Russia has been mainly associated with the defense industry over a long period, many Russian latest publications represent studies accomplished earlier in the past.

2. Marine application of titanium

By the term "marine application" is basically meant the use of titanium in construction of civil and military surface and submarine vessels as well as of other structures like distilling plants and floating power plants, where one of the basic requirements for the material is that it be good enough to work in sea water.
Marine structures can be divided into three categories: hull-type, mechanical engineering-type and power engineering-type structures. Titanium can be used to one or other extent in all these categories of structures.

2.1. Hull-type structures

2.1.1. Experience in using titanium for hull-type structures

The use of titanium as a hull-construction material is justified by its properties, such as: high specific strength, absolute resistance to corrosion in sea water, non-magnetizability, and cold resistance.
In 1968, the world's first multi-purpose nuclear-powered submarine ("Papa" class according to NATO classification) was built of titanium in Russia **(Figure 1).** Its normal displacement was 5,200 tons, length, about 100m[1-3]. It was a revolutionary step in using titanium for structures of such a big volume and weight.

Figure 1. The world's first nuclear-powered titanium submarine, Russia.

Owing to titanium, performance capabilities of similar-class submarines were improved.
During the ensuing years the design and production of nuclear-powered titanium-hulled submarines were being continued **(Figure 2).**
Between 1974 and 1981 the series of all-titanium nuclear-powered submarines ("Alfa" class to NATO specification) of 2,300 tons normal displacement and about 80m long was built.

In 1983, the deepest-diving nuclear-powered titanium-hulled submarine "Komsomolets" of 5,600 tons normal displacement and about 120m long was built. The series of nuclear powered titanium-hulled submarines ("Sierra" class to NATO classification) of 6,300 tons normal displacement and about 110m long was built from 1983 to 1992.[2]

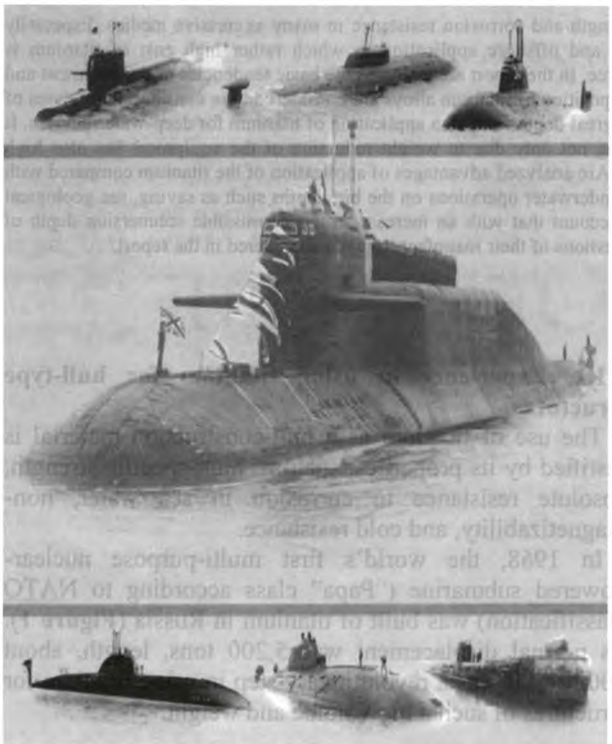

Figure 2. Submarines with titanium hull or titanium-made equipment., Russia.

In 1988, the diesel-driven titanium-hulled little submarine "Pirania" of about 220 tons normal displacement and about 30m long was built. She was presented at International military technology exhibition in Abu Dhabi (United Arab Emirates) in 1993.

In 1990s the series of deep-sea titanium technical stations of about 1,500 tons normal displacement and 40 to 60m long was built[2].

In the 1995-2005 time frame, the series of titanium manned submersibles (project "Rus") displacing about 25 tons and diving to a depth of 6,000 to 7,000m with spherical pressure hull of about 2m in diameter was built **(Figure 3)**[4].

The scope of uses of titanium for building the ship hulls in other countries as compared to Russia over the same time periods was rather moderate: titanium was mostly used to build hulls of manned and unmanned submersibles with comparably small displacement of 13 to 30 tons and diving depth of 4,000 to 6,000m. These are "Alvin", USA, 13.5 tons, 1973; "Nautile", France, 18 tons, 1983; "Sea Cliff', USA, 29 tons, 1984; "Shinkai", Japan, 1989.

It should also be mentioned that titanium is used for building the hulls of small surface vessels. For example, in Japan, a yacht with titanium hull 17m long was built in 1985, and one yacht and two fishing vessels of 4.6 to 5.3 tons displacement and 12.5 to 14m long were built between 1997 and 1999 **(Figure 4)**[5,6]. In Italy, with the participation of Russian specialists, a titanium-hulled yacht 8m long was built in 1993 **(Figure 5, 6)**[7]. Titanium was also used for manufacturing foil arrangement system for hydrofoil vessels which, by their performance, fall into hull structures.

In Russia, in 1983, one of the sea-going passenger hydrofoil vessels, "Kometa"-type, was fitted with titanium forward foil as an alternative to that of stainless steel **(Figure** 7).

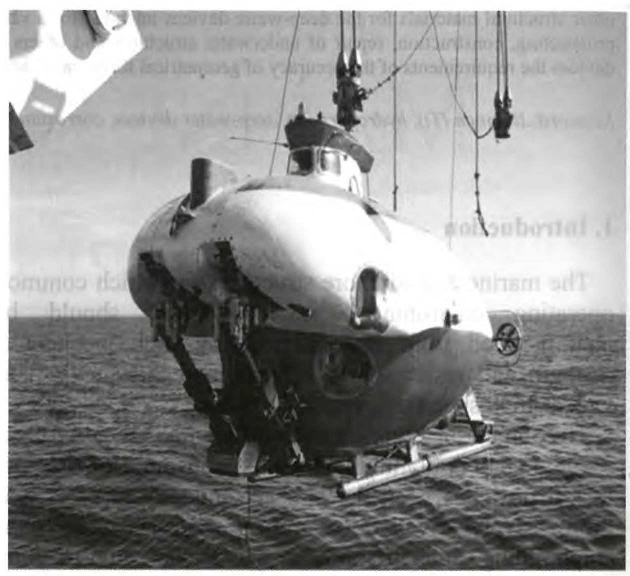

Figure 3. Submersible "Rus" with pressure hull and outer cell made of titanium, Russia.

Figure 4. Titanium fishing vessel, Japan.

Figure 5. Titanium hull of yacht, Italy.

Figure 6. Titanium framing and hull plating of yacht, Italy.

Figure 7. Sea-going passenger hydrofoil vessel "Kometa" with titanium foils, Russia.

The struts and lifting planes were made solid. Total weight of the foil was 2 tons.

The titanium foil was secured to the aluminum hull with the help of titanium fasteners and nonmetallic spacers to protect aluminum against contact corrosion.

The vessel was successfully operated by Russia at the Black Sea from 1983 till 1989 and since 1990, by Greece at the Mediterranean.

Over the period from 1990 to 1995, produced of titanium in Russia were forward and aft foil arrangements for eight "Kometa"-type passenger hydrofoils operated by Greece at the Mediterranean (**Figure 8).**

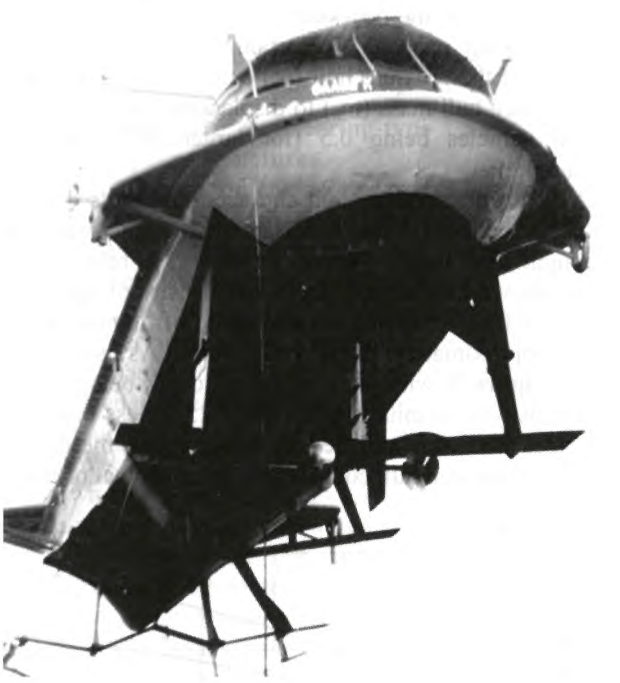

Figure 8. Fore and aft titanium hydrofoil arrangements of "Kometa"-type vessel, Greece.

From summarizing the above examples of application of titanium for hull structures, the following tendencies can be revealed. In Russia, the scope of application of titanium for the hulls of large-displacement submarines contracted drastically since 1990s, and since the beginning of the 21st century, titanium was used essentially only for the hulls of small-displacement submersibles. The latter is the line of application of titanium in construction of underwater vessels in other countries.

The way of using titanium as a hull material for surface vessels has not changed: it is individual construction of small-displacement boats for fishery and recreation businesses.

The sharp decrease in the scope of application of titanium for construction of submarine hulls can mainly be attributed to profound political and economical alterations that took place in 1990s both in Russia and in the rest of the world: disintegration of the USSR has taken place, followed by a great drop in the economical potential of the country, termination of the "cold war", changes in the world's military-strategic situation and accordingly revision of prospects of evolution of the Russia's Navy. Because of the need to save the budgetary funds, the cost of ships had to be cut, and a number of ships under construction had to be reduced.

2.1.2. Advantages of titanium for hull structures

The suspension of using titanium for submarine hulls may result in certain savings in funds. But for the deep-sea submersibles with diving depth of 2,000 to 6,000m and more, only using of titanium ensures both technical and economical advantages.
To get the required working diving depth for submersibles at the necessary reserve of buoyancy and load-carrying capacity, a certain minimum value of density of the pressure hull (p_h) determined as the ratio of pressure hull mass (m_h) to displacement (V_h) and for small vehicles being 0.5 (for larger, 0,7) must be ensured [8].
Mass of the pressure hull and accordingly its density can be reduced if the materials with higher specific strength are used. **Figure 9** shows a relationship between working diving depth and density of spherical pressure hull made of steel and made of titanium alloy with approximately equal yield point. As is evident from **Figure 9,** with working diving depth being equal, the density of titanium hull is 20 to 25 % less than that of steel, and with hull density being equal, the diving depth of titanium hull considerably exceeds that of steel.

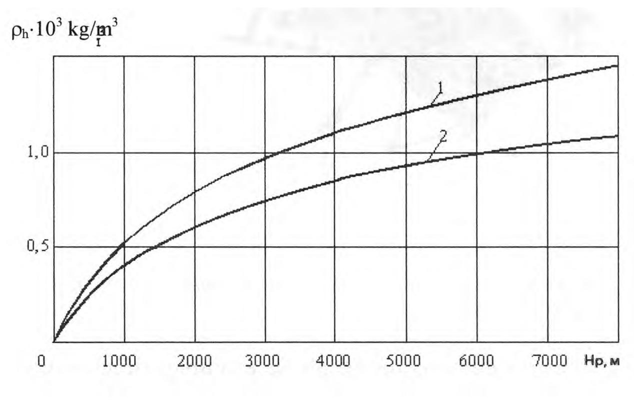

Figure 9. Density of spherical pressure hulls (p_h) versus working diving depth (H_d).
1— steel ($\sigma_{0.2}$ = 1070 MPa); 2- titanium alloy ($\sigma_{0.2}$ = 950 MPa)

2.1.3. Engineering aspects of manufacturing of titanium hull structures

For pressure hulls of submersibles, the most severe are the requirements to the accuracy of their manufacturing, because the accuracy of geometrical forms of the hull significantly affects working diving depth **(Figure 10)**[9].
By now a certain optimal standard on the form and geometrical proportions of deep-diving submersibles has been established worldwide. The manned pressure hull is defined as a sphere 2.0 to 2.1 m in diameter, where a crew of two or three as well as controls and life-support equipment are accommodated. The rest of the equipment is placed outside of the manned hull.

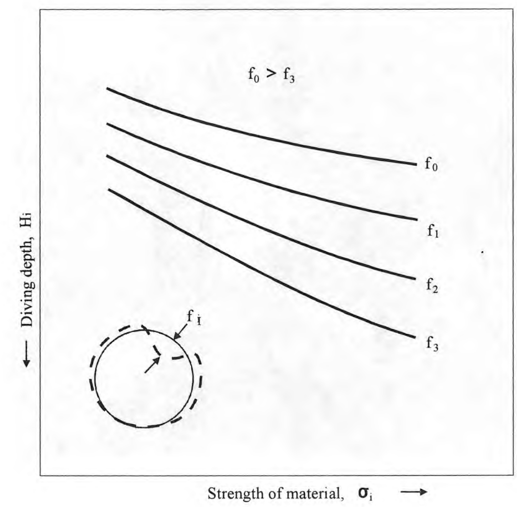

Figure 10. Diving depth versus accuracy of manufacturing (camber f_i) and strength of material (σ_i).

The most reasonable technology is that the spherical pressure hulls are manufactured from separate spherical segments which are welded together. The abovementioned stringent requirements to the accuracy of spherical form give rise to the appropriate requirements to the accuracy of manufacturing of segments as well as to assembly and welding technology ensuring the least welding deformations.
To minimize welding deformations, welding processes with small volume of smelted or built-up metal are used. Besides, since after being welded over inner and outer surfaces the spherical pressure hulls are machined, the welded joints should match the base metal in strength without weld reinforcement. The above requirements on minimal welding deformations and uniform strength are met by electron-beam welding and by argon-arc welding with filler material over the narrow gap[10].
For example, the spherical body of deep-diving submersible "Shinkai", Japan, was manufactured with the use of electron-beam welding, whereas the spherical bodies of "Rus" - type vehicles, Russia, were made with the use of argon-arc welding over the narrow gap.
With electron-beam welding, the strength of the weld metal which is smelted base metal is the same as that of the base metal.
With argon-arc welding with the use of filler material, the strength of the weld metal is generally less than that of the base metal. However, the narrow gap serves to stimulate the effect of contact reinforcement, and with an appropriate width of the weld, the uniform strength of the welded joint and the base metal is achieved **(Figure 11)**.

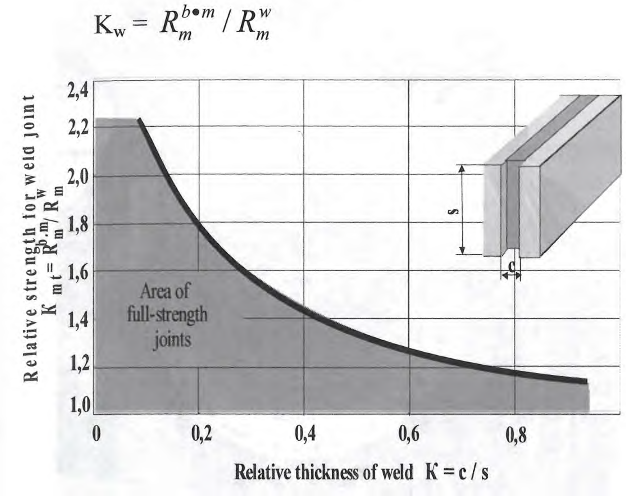

Figure 11. Diagram of limits of uniform strength of narrow gap unreinforced welds. Area of joints with uniform strength

$R_m^{b\bullet m}$ – ultimate strength of base metal;

R_m^w - ultimate strength of weld metal;

c - width of weld;

s - thickness of base metal.

2.1.4. Titanium alloys for hull structures

Titanium alloys which are used for manufacturing of hull structures should not only meet the requirements for high mechanical properties and resistance to corrosion in sea water, but should feature good weldability and adaptability to various kinds of heat treatment and machining as well.

To this end, special-property marine titanium alloys, which fall into the group of middle-strength alloys and meet the above-stated requirements, were designed in Russia. These are near-α-alloys with certain limited content of α and β isomorphous-stabilizing elements.

Among these are the most widely used in Russia alloy PT-3V compositions Ti-4Al-2V ($\sigma_{0,2}$ no less than 580 MPa) and alloy PT-5V compositions Ti-5Al-1.5V-1.4Mo ($\sigma_{0,2}$ no less than 740 MPa) which, according to the diagram shown in **Figure 12,** fall into the group of marine alloys featuring high corrosion-mechanical properties, and good weldability[11,12].

Alloys of similar class are also in use in other countries. The most widely used is Grade 5 composition Ti-6Al-4V (for example, submersible "Nautile", France) and its modification Grade 23 composition Ti-6Al-4VELJ (submersible "Shinkai", Japan) differing from the first by higher purity. Pressure hulls of submersibles "Alvin" and "Sea Cliff", USA, were made of alloy Ti-621-08 (Ti-6Al-2V-1Ta-0.8Mo).

These compositions also fall into the group of middle-strength alloys according to classification diagram given in **Figure 12** and lie in the same area as Russian

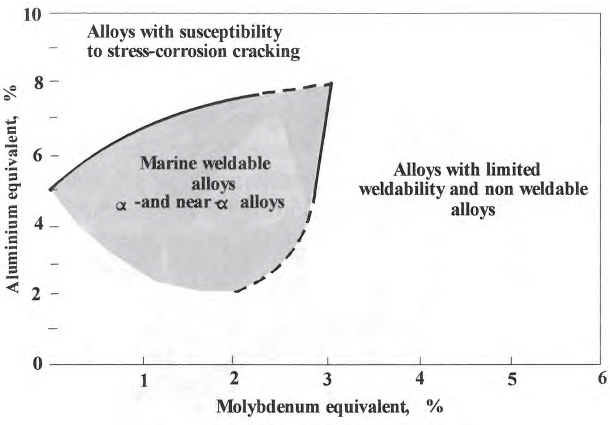

Figure 12. Limits of alloying for marine weldable titanium alloys.

2.2. Mechanical engineering-type and power engineering-type structures

A good portion of engineering structures (devices, systems, machinery) on board the above-mentioned Russia-made titanium-hulled submarines and submersibles was made of titanium as well. These are propellers and shaft lines, rudders, high-pressure air bottles, various piping systems, valves, pumps, fasteners, and others[3]. At the present time many titanium engineering structures are also in use on steel-hulled submarines and vehicles as well as on surface vessels[6,11].

Shown in **Figure 13** as an example is a standard valve of sea-water piping system, which is in use in Russia on surface and subsurface ships, and in **Figure 14,** a jet propulsion unit straightening apparatus. In the USA, main and auxiliary sea-water fire-fighting systems on board LPD-17-class ships were fitted with titanium pipes. For this purpose, NGSS company, in Avondale, of Louisiana, fabricated over 50,000 feet of Grade 2 titanium piping[13].

The 22nd ITA Conference "Titanium 2006" held in San Diego (USA) in October, 2006, showed, that titanium has been successfully used in the USA Navy in surface ship and submarine machinery systems with total weight of titanium of 16,500 to 136,650 lb per ship.

Figure 13. Titanium body of valve

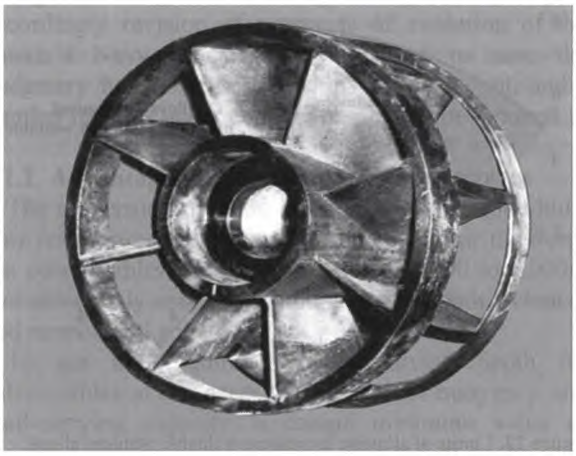

Figure 14. Titanium straightening apparatus of jet propulsion unit.

In Russia, widely used for piping systems are chemically pure titanium close to Grade 2 ($\sigma_{0,2}$ no less than 210 MPa) and alloy PT-7M composition Ti-2Al-2.5Zr ($\sigma_{0,2}$ no less than 370 MPa).

The use of titanium made it possible not only to reduce significantly the weight of equipment and machinery but also to improve their serviceability and to increase service life.

It should be specially noted the use of titanium in manufacturing steam generators, condensers, different types of heat exchangers, circulating pumps, piping systems, stop and cutoff valves and others for marine water-cooled and water-moderated nuclear powerplants **(Figure 15)**.

Titanium has the unique properties that make it possible for it to work good in nuclear powerplant environment, namely:

— high radiation resistance at temperatures from 250 to 400°C;

— a poor ability to absorb radiation and a good ability to rid itself fast of induced radiation;

— high resistance to corrosion in water and steam at temperatures up to 400°C under the conditions of exposure to radiation;

— high short-term and long-term strength at temperatures up to 400°C without corrosion or mechanical failures.

Figure 16 shows the mechanical properties of alloy Ti-2A1-2.5Zr as a function of radiation dose in reactor channels on Russian nuclear-powered icebreakers " Arktika" and "Sibir"[14)].

It is evident that the strength and plasticity characteristics of the alloy do not practically vary with radiation dose up to the value 10^{20} neutron/cm^2.

From these relationships it follows that titanium is identical to steels used for nuclear powerplants.

Figure 17 shows the curves of the fall, down to 10^{20} neutron/cm^2, in induced radioactivity for titanium and iron after their exposure to neutron flux carrying energy of more than 0,5 MeV[14)].

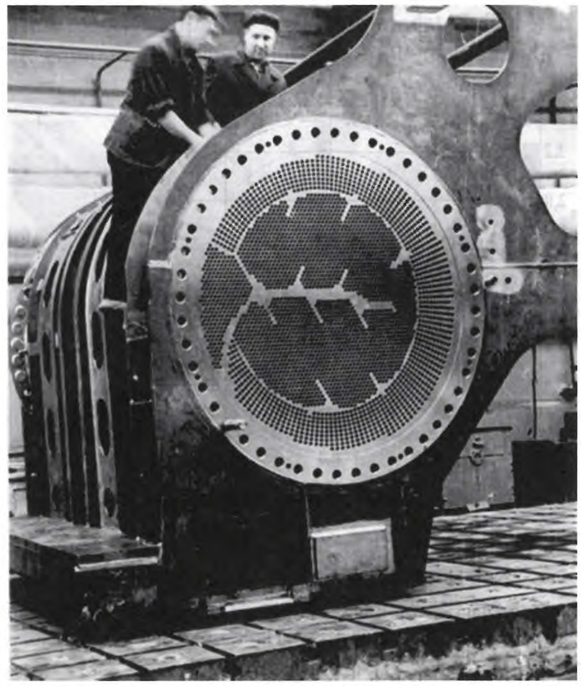

Figure 15. All-titanium condenser for ship's powerplant.

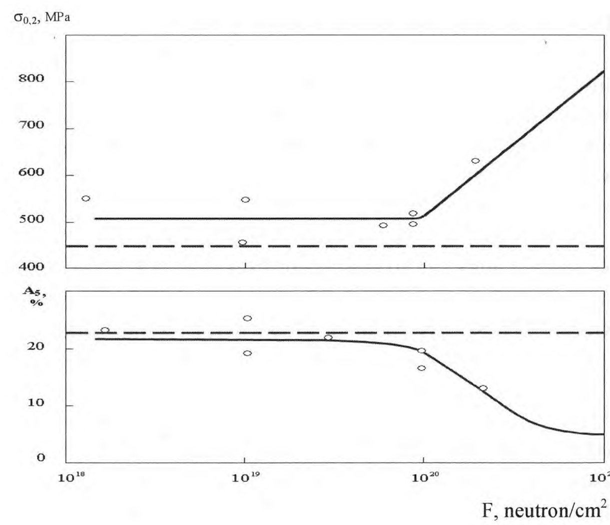

Figure 16. Mechanical properties of alloy Ti-2A1-2.5Zr versus radiation dose;
— — — — without exposure.

Neutron fluence of such magnitude generally attacks nuclear powerplant materials in the area exposed to neutron fluxes during 30 and more years depending on flux density.

As it follows from **Figure 17,** titanium, at equal neutron fluence, is characterized by much less value of induced radioactivity and higher rate of its fall comparing to iron. In rate of the fall in induced radioactivity to safe values titanium is 10 times superior to iron. That means that salvaged titanium may be recycled as a structural material in several years after exposure.

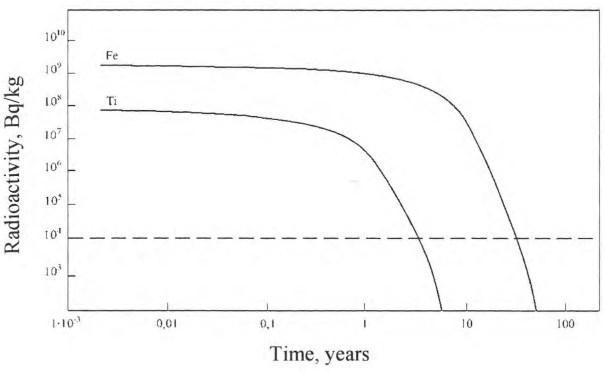

Figure 17. Calculated curves of the fall in induced radioactivity for titanium and iron after their;
- - - - - - - - exposure to radiation.

This fact is particularly important in the context of aggravation of ecological problems associated with burial of radioactive waste and salvaging of equipment of nuclear powerplants including that of marine service.

3. Offshore application of titanium

By offshore application of titanium is meant that it is used for oil-and-gas production complexes which include offshore structures and ocean engineering facilities for exploration for hydrocarbons, for extraction, and transportation of hydrocarbon raw from oil-gas fields. Depth of the sea at the shelf which is presently subject to major commercial development of oil-gas fields may vary over wide limits, down to 2000m.

In contrast to seagoing objects, operating conditions for offshore oil-gas production equipment are more complicated due to the following major factors:

— presence of corrosive medium in the form of oil, gas, brine water, drilling mud carrying hydrogen sulphide, carbon dioxide, oxygen and other impurities;

— elevated temperatures, from 150 to 200°C;

— drilling mud-associated products resulting in erosion ware (sand et al.) and moving at a rate of 30 m/sec;

— high internal pressure of the medium;

— big static and dynamic loads due to wind and waves, northern ice field pressure, seismic loads in seismic-active production areas;

— lowered ambient temperatures, down to -50°C.

Titanium can be used in various oil production systems and facilities. For underwater duty: these are drill pipes, underwater risers, body structures of deep-water engineering facilities and others; for surface duty (on platforms) these are sea water and drinking water systems, various heat-exchanging equipment (distillers, steam generators, coolers), pumps, fire-extinguishing systems and others. The biggest experience in using titanium alloys in European offshore industry was It is known, for example, that titanium is abundant in oil production platforms working on Norwegian shelf, in amounts of more than 500 tons per platform.

Russia has little experience in using titanium in offshore industry because currently the country is through the preliminaries to the beginning of active development of its hydrocarbon reserves on Arctic and Far East shelves. To develop oil and gas resources in Arctic, Russian and Norwegian companies are drawn into co-operative organizations. The International symposium "Enterprise Barents-2006" held in June, 2006 in Arkhangelsk, Russia, showed that Norway is becoming a strategic partner of Russia in progressing of hydrocarbon production in the north.

It is believed that titanium alloys should find rather extensive use in development of Arctic oil-gas fields (Pryrazlomnoje, Shtokmanovskoje, Rusanovskoje, Leningradskoje and others). As this takes place, all titanium structures designed for offshore application could be produced by Russian manufacturers **(Figure 18)**.

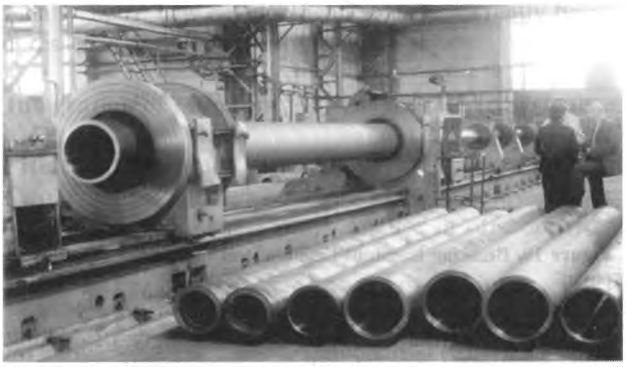

Figure 18. Titanium pipes for risers. PSC "Corporation VSMPO-AVISMA", Russia.

As of now, in the design of the platform for the shelf oil field "Pryrazlomnoje", Arctic, provision is made for the use of titanium for piping network in amount of about 350 to 400 tons, with a portion of piping being supposed to be subjected to surface thermal oxidation to protect the steel structures of the platform against bimetallic corrosion.

The 6th Pacific/Asian International symposium on offshore engineering "ISOPE PACOMS-2004" held in Vladivostok (Russia) in May, 2004 showed that in joint (Russia, the USA and Japan) development of oil-gas fields on Sea-of-Okhotsk shelf, Far East, titanium was not practically been used in projects "Sakhalin - 1, 2". This fact is primarily attributed to the presumed relatively short period of operation of equipment in these fields.

With progress in offshore oil production, the demand for the use of titanium alloys for manufacturing of equipment will increase fast.

Titanium will grow in importance with the increase of depths oil and gas is extracted from, because drilling at

great depths implies a reduction in mass of drilling systems.
For the heavy steel drilling systems the supporting substructures for platforms has to be more massive and the hoist more powerful than for titanium equipment.
Figure 19 shows comparative data on breaking length of steel and titanium pipe string, that is, the length at which the pipe may break under its own weight. As can be seen from **Figure 19,** with the same yield point the breaking length of titanium pipe string is far greater than that of steel pipe. That means that with the same weight characteristics the titanium piping systems can be used in deeper oil-gas fields than the steel ones.

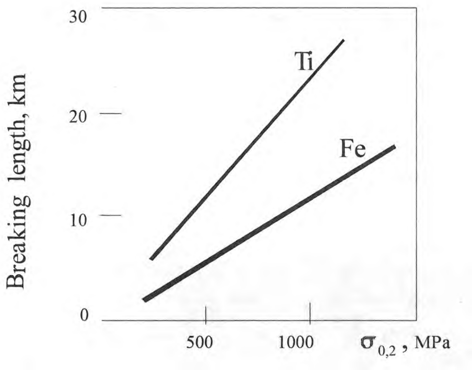

Figure 19. Breaking length of titanium/steel pipe string versus yield point.

Using of titanium in displacing structures of drilling systems also has big advantages. For example, using of titanium for risers makes it possible to reduce the density of structures and to increase thereby their buoyancy or, like with submersibles, working depth.
The problems of offshore hydrocarbon production are aggravated not only by depths of the ocean but also by the oil-and-gas reservoir depth. For example, the gas-condensate field "Shtokmanovskoje" in Barents Sea (Russia) lies at depths of 280 to 380m, whereas gas-condensate reservoirs are in a depth range of 1,800 to 2, 300m.
As boring has to be carried out under severe geological conditions, the requirements on specific strength, thermal conductivity, and resistance to wear are becoming more rigid.
For the objects of offshore industry Grade 5 (Ti-6Al-4V), its modification Grade 23 (Ti-6Al-4VELJ) as well as Grade 9 (Ti-3Al-2.5V) alloys are mostly used worldwide.
Taking into account the hostile activity of the medium and elevated temperatures, it is possible to use the above alloys modified by adding Palladium and Ruthenium, that is, Grade 24 (Cr.5+0.5Pd), Grade 29 (Cr.23 +0.10Pd) , Grade 18 (Cr.9+0.5Pd), Grade 28 (Cr.9 +0.10Ru) alloys[14)].
For Russia's offshore industry it is recommended to use marine titanium compositions Ti-4Al-2V (PT-3V) and Ti-5Al-1.5V-1.4Mo (PT-5V). If they have to be used in more aggressive media and at elevated temperatures, it is recommended to modify them by adding small amount of Palladium and Ruthenium[15)].
In conclusion, some considerations about the reasoning behind the use of titanium in connection with its rather high cost are suggested. In deciding on a material for the structures, specifically, for marine or offshore application, the designer faces the alternative: to choose either cheep but inadequately long-lived material or more expensive but a long-life one. A cheep material is more economical in first costs but makes service more complicated due to frequent maintenance and downtime. A more expensive material involves more investments but reduces operation costs.
The use of titanium instead of other structural materials is completely justified because higher acquisition cost of titanium equipment is compensated for by its long service life and low operation costs.

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