Application of cylindrical covers from glass-metal composite made by spin casting method for strong cases of deep-sea submersibles

V K Goncharuk¹, A A Bocharova², A A Ratnikov²

¹ Institute of Chemistry of FEB RAS, 159, Stoletiya Av., Vladivostok, 690022, Russia
² Far-Eastern Federal University, 8, Sukhanova St., Vladivostok, 690950, Russia

E-mail: pmm-fentu@mail.ru

Abstract. In this work the manufacturing techniques of layered constructional material metal-glass-metal are considered by method of centrifugal casting; a similar approach to formation of a glass layer without superficial microcracks has no analogues in the world practice. The scheme of installation for production of cylindrical covers from a glass-metal composite is provided. The research of the main technological modes providing reliable connection of aluminium coverings with the glass which is in a plastic state is conducted. Optimum values of temperature parameters are defined. Methods of electronic microscopy have investigated the diffusive layer which is formed on the glass-aluminium border.

1. Introduction

World experience of submersibles exploitation proves that it is impossible to imagine rescue and search operations, hydrographical and biological research, exploration of oil, gas, metalliferous sand and concretions, main laying and assembling of underwater oil storage, maintenance and repair of different underwater structures without it. With the help of unmanned robotized submersibles one can search and inspect sunken objects and artificial structures, do geological exploration and bed mapping, carry out work while building and exploiting of hydraulic structures, underwater cables, pipe lines and other objects. The main and crucially important problem of shelf exploration is devices delivery for seabed research to deep sea where it is impossible to use conventional diving equipment. The significant trends for modern submersibles are submergence depth and deadweight increase. Due to a growing demand for underwater works new, more advanced submersibles with an increased submergence depth up to 6000 – 6500 metres are developed, new requirements to submersibles functional qualities appear in terms of their self-sufficiency, speed and payload capacity increase. With the expansion of research programs and works in the World Ocean in various cavities and faults, which are not explored at the moment, there appears a task to create submersibles for working at the depths more than 6500 metres, which demands further increasing of vessel materials durability. Improving competitiveness of upcoming underwater means of transport demands application of principally new construction materials with significantly improved operational features.

The creation and application of construction composite materials is a domineering concept of modern material engineering development. Experimental investigations in this field show that glass and glass ceramics are vastly superior to such construction materials as steel, aluminium and titanium
alloys in terms of compression strength-weight ratio. Silicate glass reach durability of around 10 hPa exceeding titanium alloys durability by an order of magnitude. The investigations of glass atomic structure in the process of destruction have determined the main conditions, the adherence to which contributes to an unusually high durability of the glass: getting rid of surface microdefects increases glass durability by an order of magnitude; elimination of interference between glass and moisture in the air increases durability 2-fold; elimination of inner microdefects increases glass durability by 30%. As a result of these conditions, adherence the durability of damage-free non-organic glass approximates its theoretical level.

The principal material of this kind is invented in the Far East (by V.V. Pikul); this is a new composite nanomaterial on the basis of glass – glass-metal composite, which represents a new class of composite construction materials unparalleled in the world. The received approach to forming glass layer without surface micro cracks cannot be compared to anything in the world practice of surface micro cracks elimination in the glass. By now, 13 RF invention patents (№№ 2196747, 2243900, 2244655, 2337036, 2361770, 2361771, 2425776, 2433969, 2491202, 2497709, 2505495, 2567584, 2578905) have been received for different ways of manufacturing different items from glass-metal composite.

Glass-metal composite is a layered composite material (metal-glass-metal), in the process of manufacturing of which an outer metal shell, glass layer and inner surfacing are formed layer by layer from metal melt and glass with the help of centrifugal casting method. Concurrently, in the composition of glass-metal composite all three main conditions of defect-free silicate glass structure are realized. An outer metal shell firmly connected with a glass layer while cooling, due to a higher thermal expansion coefficient, decreases its dimensions more intensively than the glass layer, thus retracting the surface of glass layer, preventing extension strains and excluding surface micro cracks. Outer and inner shells exclude immediate contact of the glass layer with external environment, isolating it from moisture and other negative effects. Inner defects are eliminated by the forming glass layer under the pressure. As a result, in the glass-metal composite composition there forms a defect-free glass layer with spatial nanostructure, which results in the fact that the material in general gets a high durability and impact endurance.

In order to manufacture durable carcasses of deep-sea submersibles, the materials with a high strength-weight ratio, corrosion resistance and handling properties are in need. To the fullest extent these requirements are met by titanium alloys. High endurance aluminium alloys also have a high strength-weight ratio, but in comparison with titanium alloys have a lower corrosion and handling properties. Glass-metal composite is an advanced material for durable carcasses of submersibles from the perspective of their durability, stability and manufacturing cost in comparison with the carcasses from titanium alloys used nowadays for works at great depths. High durability of glass-metal composite in case of small weight enables to create deep-sea submersibles, which can work at ultimate depths of the World Ocean without using additional volumes of flotation [1-3]. The goal of this work is to study technological operations modes of cylindrical shells manufacturing using centrifugal molding on the laboratory facility in order to determine an optimal temperature of glass melts filling, temperature of metal shells, providing durable connection of glass and metal, to examine the parameters of the intermediate layer, which is originated due to diffusion on the metal-glass borderline.

2. Problem Statement

Primarily silicate glasses are considered as a glass layer in composite materials of metal-glass-metal type as they are most widespread and studied. The main requirements for the glass, which is used for the glass layer, are: construction with three-dimensional joining of structural elements (structural factor) and melt viscosity in the operating temperature range (processing factor). On the one hand, glass with the maximal degree of structural elements joining into a three-dimensional net is notable for the greatest durability, which is favorable for products mechanical strength increase. On the other hand, glass melts of such structure have an increased viscosity, which makes the manufacturing of
metal-glass-metal composite materials difficult including the method of centrifugal molding. The transformation of liquid glass melt into a product of a desired configuration is carried out by a combination of fluidity of glass melt with its continuous solidification, which is characterized by viscosity intensification while cooling. That is why forward estimate of optimum relationship of the above mentioned factors to choose composition of glass, the viscosity of which melt could manufacture the products of high durability, is necessary. The experience of glass-metal composite shells manufacturing shows that melt viscosity must be lower than 10 P, that is why the main goal while choosing a formulation of silicate glass is to find additives, which, on the one hand, would decrease viscosity, and, on the other hand, would not destroy a three-dimensional joining of the net, in other words would not decrease glass durability substantially.

Steel, aluminum and titanium alloys are mostly used as construction metals nowadays. Ultimate deformation of construction metals for the break decreases while durability increasing. However, due to exceptionally high durability of defects-free silicate glass, the durability of metal shells for glass-metal composite is a secondary factor. Their plasticity has a greater importance. Low carbon steel and low durable types of aluminum and titanium alloys have an increased plasticity, besides, they are much cheaper than highly durable brands of construction metals. In the present study aluminum and silicate glass were chosen as metal for metal shells because they have a chemical affinity.

3. Pursuance of the Research

In order to manufacture layered aluminum-glass-aluminum cylindrical shells by a method of centrifugal molding a laboratory facility was created. The plan is provided in fig. 1.

![Figure 1](image_link)

**Figure 1.** The scheme of manufacturing glass-metal composite cylindrical shell: 1 – outer metal lining; 2 – glass layer; 3- inner metal lining; 4 – butt end metal linings; 5 – form; 6 – centrifuge

Manufacturing of cylindrical shell is performed the following way. A preliminarily prepared for joining with the glass layer outer metal shell and metal butt ends are put into form 5 and heated up to the temperature of 400 – 500 ºC and put into the centrifuge. While the centrifuge is rotating, the glass melt is handed inside the form at the temperature of 1400 – 1500 ºC in order to form a glass layer, on the assumption of getting a glass layer of 5 mm. The temperature of glass layer is lowered up to 800 ºC, which provides its durable connection with metal alloy of the inner metal lining 3, then metal alloy heated up to 800 ºC is handed to a glass layer to form an inner lining. Using centrifugation, a necessary thickness metal shell (1 mm) and glass layer (5 mm) are formed.

In order to provide equal thickness of glass-metal composite glass layer a cylindrical shell is cooled up to the temperature of glass transition of glass layer (550 ºC) while working centrifuge, then annealing of cylindrical shell is performed under the temperature of glass transition up until a full strain relaxation and stabilization of the glass layer properties.
In the process of glass-metal composite cylindrical shell formation a glass melt, having a temperature of more than 1400 ºC, cools down to normal temperature (20 ºC). While the temperature is lowering, glass melt is transforming from liquid state to viscoelastic state, then to viscoelastic and, finally, to solid (fragile) state. With that at the borderline of metal-glass there is forming of transitional diffusion layer.

4. Study Results
As a result of the studies of glass-metal adhesion quality dependence on the temperature of glass filling, on the temperature of aluminum shell the optimal conditions of filling were determined with the centrifuge rotation speed of 4000 rotations/minute for the chosen measures of the shell: minimal temperature value of glass melt filling – 1450 ºC and starting temperature of aluminum shell before filling - 300 ºC. The durability of connection is provided due to forming of diffusion layer on glass-aluminum borderline, having thickness of 2-4 micrometers and eliminating surface micro-defects of the glass. The investigation of the interlayer was held with the help of modern means of electronic scanning microscopy.

The investigation of the diffusion layer on aluminum-glass borderline was held with the help of Hitachi TM-3000 electronic microscope completed with energy-dispersive extension for micro-analysis. In Fig. 2 – 4 there are pictures representing the borderline of aluminum –glass with different magnifying.

High strength indexes of glass-metal composite cylindrical shell are accomplished basically by means of the formation of transitional diffusion layer on aluminum-glass borderline and elimination of surface micro-cracks in the glass layer.

The analysis of micro-photographs (fig. 2-4) shows that the penetration depth of glass into aluminum reaches values of around several micro-meters and the diffusion layer is uneven and ulterior. Aluminum surface is also heterogeneous. While magnifying 1500 times, aluminum inclusions are seen in the glass layer, moreover, the sections of such inclusions have the same squares. This is indicative of the transition layer formation having its own structural characteristics. Otherwise, the surface of the separation would be mainly filled either with aluminum or glass.

![Figure 2](image1.png)
**Figure 2.** General view of glass-metal composite slice with clearly visible aluminum-glass borderline while magnifying 250 times

![Figure 3](image2.png)
**Figure 3.** Glass-aluminium borderline while magnifying 500 times
Figure 4. Glass-aluminium borderline while magnifying 1500 times

With the help of Shimadzu energy-dispersive X-ray fluorescence spectrometer series EDX 800 HS an elemental analysis on glass-aluminum borderline was held. This has given an opportunity to determine the thickness of transitional diffusion layer more precisely. Fig. 5 represents the distribution of elements concentration included in the composition of glass and aluminum on glass-aluminum borderline.

Figure 5. Distribution of elements in glass-metal composite in transitional diffusion layer on aluminum-glass borderline. Values presented on axis of abscissas are in micro-meters

5. Findings

Usage of modern measuring tools has enabled to hold the investigation of optimal manufacturing conditions and parameters providing a substantial joining of glass layer with metal linings and to obtain new scientific results for glass-metal composite manufacturing technology realization. In the process of glass-metal composite three-layer shells manufacturing at the laboratory facility a high quality of cylindrical shell layers joining was obtained under optimal conditions of filling in comparison to the results published in foreign works on other ways of joining glass and metal [4 – 6].

The results of the calculations performed on the basis of the developed methodology of submersibles durable carcasses engineering and analysis demonstrate that in case of equal resistance to buckling failure glass-metal composite shells are 1.4 times lighter and have 1.5 more cargo load than the shells from highly durable titanium alloy. Rigidity value for glass-metal composite is – 29.4 mPas·m³/kg and this is 30-40% higher than for titanium; at the same time glass-metal composite shells
are more than 8 times cheaper because they are manufactured from raw materials being in unrestricted amounts. Cargo load of glass-metal composite submersibles durable carcasses designed for working at 6 000 and 9 000 m depths using in calculations glass pressure ultimate strength value comprises a value around 50 – 90 % of carcass mass. Density value in relation to outer content for the obtained glass-metal composite shells is 10 – 20% lower than the corresponding value (826 kg/m$^3$) for submersibles durable carcasses manufactured from highly durable titanium alloys, which are nowadays the most effective materials for large-sized durable carcasses. This fact confirms applied significance of glass-metal composite application in underwater vessel engineering.

References
[1] Pukh V P, Baikova L G and Kirienko M F 2005 Fizika tverdogo tela 47 850–855
[2] Pikul V V 2008 Perspektivnye materialy 3 78–83
[3] Pikul V V and Goncharuk V K 2009 Vse materialy. Entsiklopedicheskii spravochnik. 6 5–9
[4] Bocharova A A, Goncharuk V K and Ratnikov A A 2016 Proceedings of the Twenty-sixth (2016) International Ocean and Polar Engineering Conference 237–241
[5] Bocharova A A and Ratnikov A A 2015 Proceeding of the 2nd International Conference of Advanced Materials, Mechanical and Structural Engineering (AMMSE 2015) pp 210–205
[6] Fu X L and Chen Y 2014 Materials Science and Engineering