Hydrospace Materials

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The performance under high hydrostatic pressure of the most important deep submergence materials is covered by this paper. Special attention is given to materials with meaningful applications such as titanium, high strength steels and filament wound plastics for structures; buoyancy materials for use external to the pressure capsule and encapsulating materials for external machinery and components. Several novel approaches such as new techniques for welding and fabrication, methods for encapsulation and a new concept for deep submergence buoyancy systems are covered. The fabrication of high strength and exotic metals under field conditions is discussed in detail and several examples of innovative fabricating techniques are illustrated. The paper includes a look at the decade which follows and a prognosis of what can be expected from materials during this period.

Introduction

A RAPIDLY growing interest in the decade to come will stimulate science and technology to reach down towards the riches of the ocean and the ocean bottom. National recognition of the importance of the ocean has been demonstrated by the United States, which under Public Law 89-454, created the National Council on Marine Resources and Engineering Development and the 15-man Commission on Marine Science Engineering and Resources appointed by President Johnson in January 1966 and headed by Julius A. Stratten, Chairman of the Ford Foundation.

All of our efforts in the next decade will be directed to the extension of our growing competence in dealing with the ocean and the deep ocean in particular. There have been several categories established in recent years for ocean space exploration which encompass different depths. A common categorization has been as follows: a) continental shelf studies extending to 1000 ft maximum depth; b) intermediate depth 10,000–12,000 ft; and c) deep ocean approximately 20,000 ft.

It is obvious that thousands of materials problems will emerge as we attempt to go deeper into the ocean. It is also evident that the more familiar materials problems encountered on or near the surface differ from those to be anticipated at 20,000 ft. This paper will avoid touching on the many incidental materials problems that come to mind and will confine itself to an examination of the role of structural materials, buoyancy materials, encapsulating materials and special coatings.

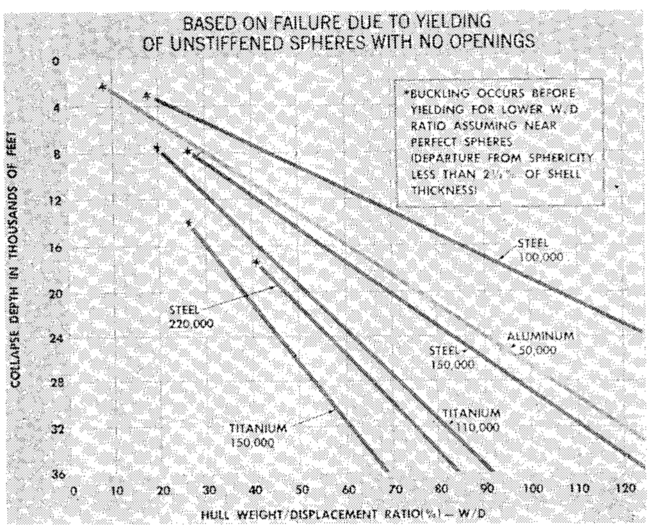

Fig. 1 Collapse depth vs buoyancy relationship for a pressure sphere of various metals.

Utilization in Hydrospace

In dealing with structural materials, Figs. 1 and 2 illustrate the potential of various classes of materials. Figure 1 covers much of the spectrum for structural metals by plotting collapse depth against buoyancy for spherical pressure hulls. The promise of titanium and the ultrahigh strength steels is illustrated by their respective low weight displacement ratios.

Figure 2 shows a similar relationship for high strength steel, titanium and filament wound plastic, in this case for a ring stiffened cylindrical hull. The promise of filament wound plastics is especially evident here. It would be appropriate

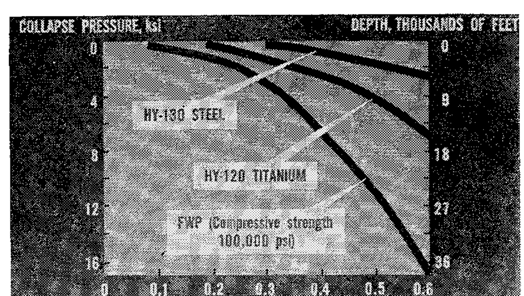

Fig. 2 Collapse depth vs buoyancy relationship for a ring stiffened cylinder of steel, titanium or filament wound plastic.

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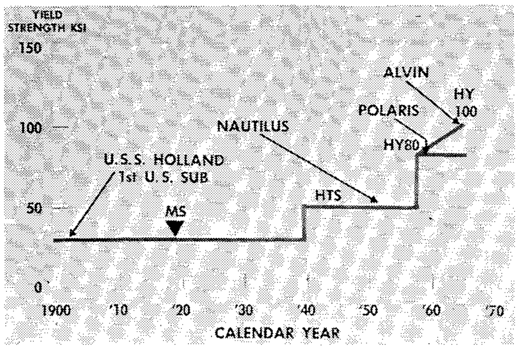

Fig. 3 Steels for hydrospace (progress to 1965).

to discuss at this point each of these three candidate materials shown in this chart.

High Strength Steels

These materials are attractive because they represent a metal that is proven and familiar to the marine designer, and because they will be competitive with the lighter metals such as titanium, when the fabrication problems for heavy thicknesses can be solved for both the quenched and tempered categories and the maraging steels of over 200,000 psi in yield strength. Figure 3 illustrates our progress in the use of steels in the Navy in this century. You will note that it is only in recent years, with the advent of the POLARIS submarine, that steels of high strength begin to appear in the submersibles programs. Figure 4 provides us with a look at the potential for the next decade. The upper limit is an optimistic estimate of steels that may be developed for certain deep diving vehicles and other specialized applications.

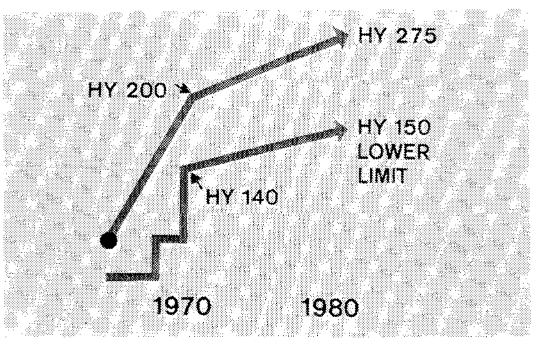

Fig. 4 Steels for hydrospace (period 1970–1980).

Some of the properties of the quenched and tempered steels currently available in heavy thicknesses are listed in Table 1. It is to be noted that although high strength steel alloys are available, one of the limiting factors in their use, in addition to low toughness, is the fabrication technology. Accordingly, we are in the process of developing techniques for successfully welding HY-180 in heavy plate under shipyard conditions. Figure 5 summarizes some of the promising experimental results attained in the welding of a 2-in. thick plate of HY-180 steel. Special processing is also improving the properties of these steels at the mill as shown in Fig. 6, which highlights the significant improvements in toughness that special processing can provide.

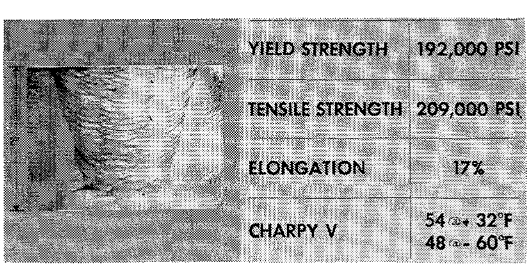

Fig. 5 Properties of experimental TIG weld of HY-180 steel 2 in. thick.

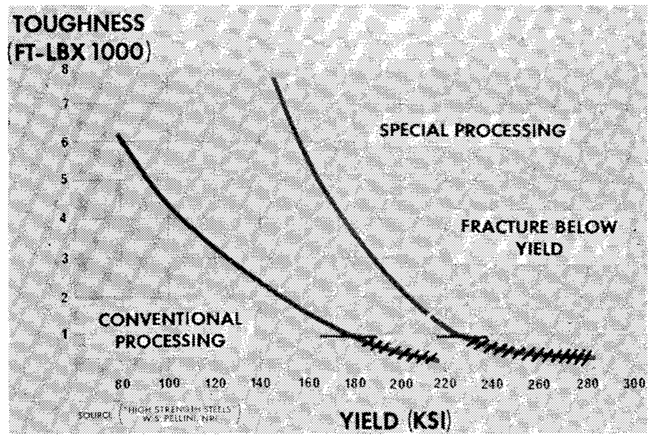

Fig. 6 Effects of special processing on high strength steels.

Titanium

For many years this material was essentially unavailable to the naval engineer primarily because its highly reactive nature made it impossible to weld in heavy thicknesses under shipyard conditions. It is true that the aircraft industry has been using titanium extensively in sheet form, fabricated under special conditions (usually in-chamber). Within the last five years the Navy has developed techniques for the welding of alloy titanium out-of-chamber in any position and in thicknesses up to 4 in. In addition, large forgings, heavy rolled plates and spun spherical heads in thicknesses up to 4 in. have been successfully produced under industrial manufacturing conditions without degradation of the base material. The welding is done by the use of trailing shields that are attached to the welding gun and provide an inert atmosphere in the vicinity of the weld. A variety of parameters have been studied and fixed, including weld wire compositions, gas quantities and types, design of trailing shields, and current

Table 1 Composition and properties of quenched and tempered steels

Steel	Nominal composition C	Ni	Cr	Mo	Yield/tensile strength (KSI)	Charpy V (0°F)
9-4-20 (Cr Mo)*	0.20	8.0	1.00	1.00	180/210	50
9-4-25*	0.25	8.0	0.45	0.45	190/200	40
9-4-45*	0.43	8.5	0.25	0.25	250/295	20
4340	0.40	1.8	0.25	0.25	240/300	15
*4 Mo, 0.1V						

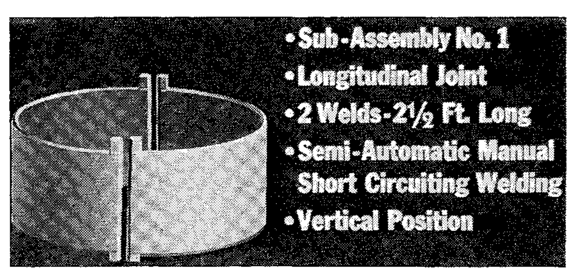

Fig. 7 Sub-assembly 1 used in welding 6000 lb titanium 721 alloy cylinder.

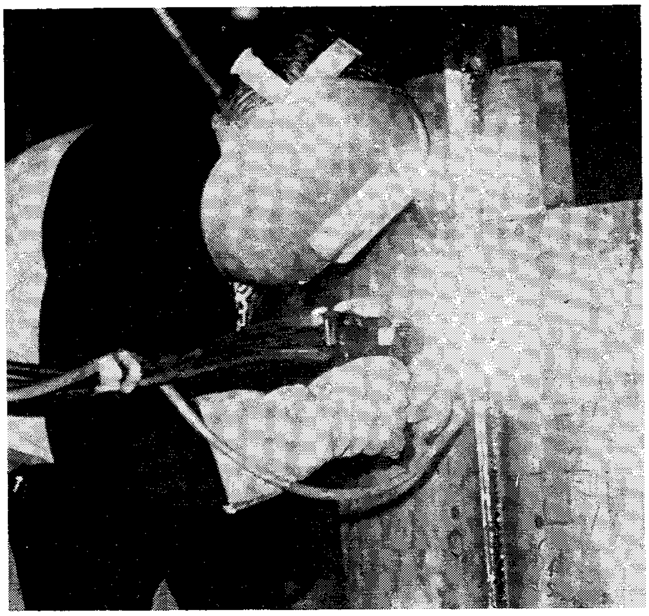

Fig. 8 Welding titanium sub-assembly under shipyard conditions.

and voltage levels. High-quality welds can be produced in most families of titanium alloys currently in use including the well-known 6Al-4V alloys used by the aerospace industry. The next series of figures illustrate a fabrication exercise that has been carried out by the Navy, and which served to demonstrate how far we have gone in the fabrication technology of massive titanium objects. This exercise was directed toward the construction of a titanium alloy cylinder 7 ft in diameter, 5 ft long and with a wall thickness of $2\frac{1}{4}$ in., fabricated from Ti-721 alloy plate. When completed, this cylinder weighed 6000 lb. Beginning with a large sheet of rolled plate obtained from the mill, several sub-assemblies were prepared. Figure 7 shows such a sub-assembly (1). Figure 8 shows the actual welding of this sub-assembly under shipyard conditions and Fig. 9 shows it in completed form. A similar second sub-

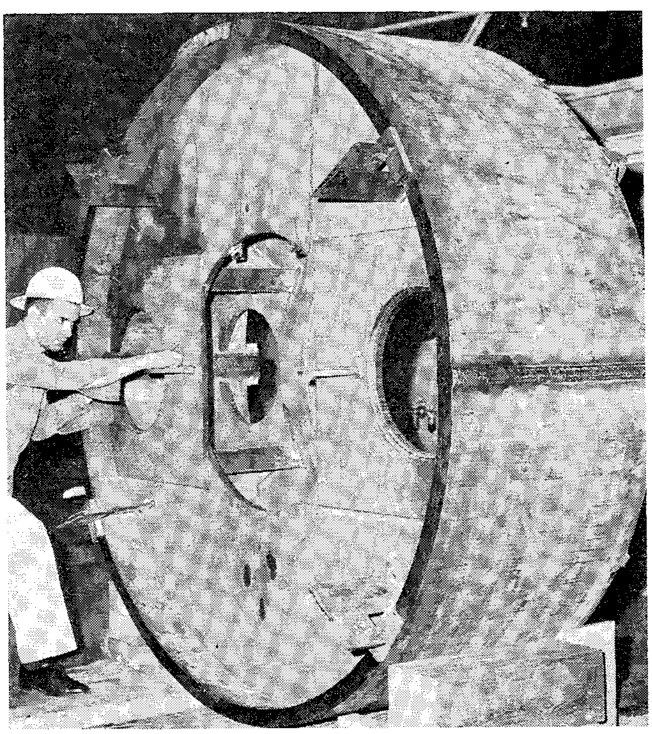

Fig. 9 Completed titanium sub-assembly 1.

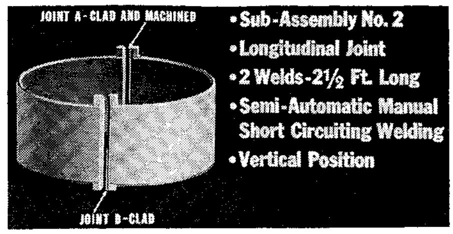

Fig. 10 Sub-assembly 2 used in welding 6000 lb titanium 721 alloy cylinder.

assembly was also prepared. Only in this case, sub-assembly 2, shown in Fig. 10, was made intentionally short so that the joint would require cladding. This cladding reduced the root opening in the sub-assembly 2. A comparison of the physical properties of the completed cylinder welds and the base plate is shown in Table 2.

Special note should be taken of the high quality of the welds on this large fabrication, which is believed to be the largest titanium alloy weldment made to date and is shown in com-

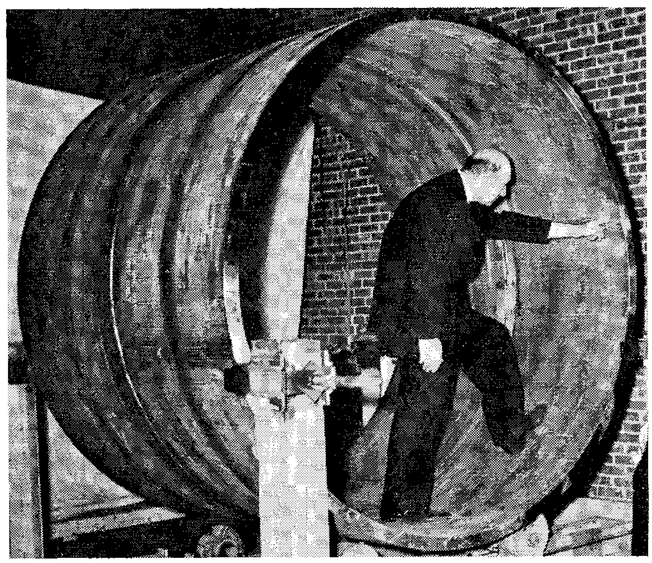

Fig. 11 Completed titanium cylinder 7 ft in diameter, 5 ft long and 6000 lb in weight.

pleted form in Fig. 11. Because of the stress corrosion cracking susceptibility of the 721 series of titanium alloys, the Navy launched a program to develop an improved alloy that would not be susceptible to this type of failure. This effort resulted in the Ti-621/0.8Mo alloys with markedly improved stress corrosion properties, shown in Fig. 12. It will be noted from this figure that these tests were conducted on both base plate and a butt weld using a large 1-in. thick plate subjected to simple bending. It is evident that the 0.8 Mo alloy, after it had been precracked, required 410 hr to cause crack growth

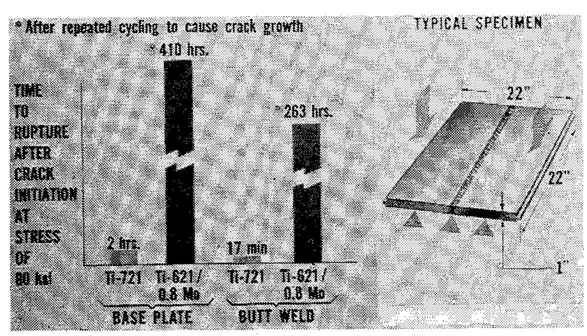

Fig. 12 Stress cracking performance of titanium alloy plate specimens in sea water.

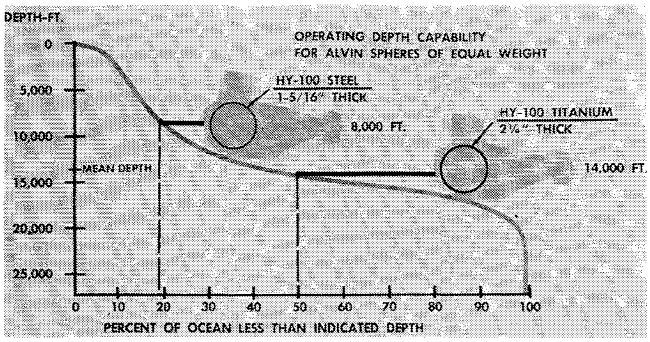

Fig. 13 Calculated comparison of performance for the ALVIN using HY-100 steel or a titanium alloy.

under a stress approximating 75% of the yield strength, and that the butt weld did not show any serious degradation over the properties of the base plate itself. Similar studies on heavy plate 6-4 titanium alloys are concurrently under investigation. There is no question that titanium is a serious contender for vehicle structural materials, especially in the 10,000 ft depth range. In a somewhat simplistic representation, Fig. 13 shows the comparison of titanium with HY-100 steel and uses the ALVIN vehicle as a basis of comparison.

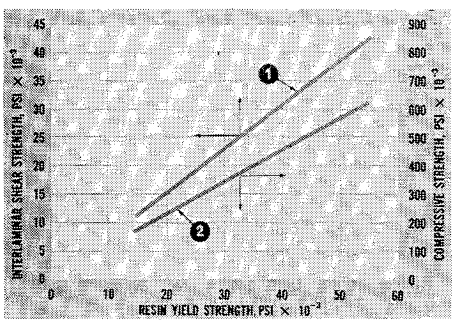

Fig. 14 Strength relationships for a glass reinforced filamentary composite. 1) Interlaminar shear strength to prevent debonding failure; 2) projected compressive strength based on resin yield.

This figure shows the increased depth capability of the vehicle using titanium, or more dramatically, the increased percentage of the ocean bottom which could be explored by the same vehicle using titanium instead of steel.

Four 7-ft diam hemispheric heads of 3-in. thick alloy titanium (Ti 6Al-2Cb-1Ta-0.8Mo), the largest ever formed, were successfully hot-press formed in a Navy project designed to provide a Navy-certified pressure hull for use in the ALVIN/AUTEC class deep diving submersible. In addition to providing an increase in operating depth from 6000 ft to 12,000 ft, the project will provide the Navy with experience in utilizing a new unproven material for man-rated pressure hull fabrication and will provide criteria for specifying the Navy's certification requirements for all new materials.

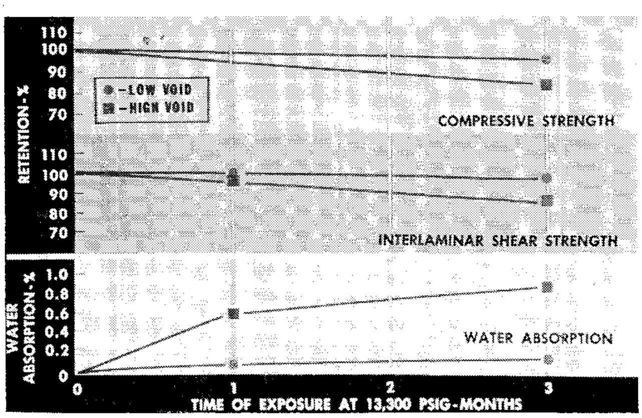

Fig. 15 Effect of void content on properties of filament wound plastics; effect of time of exposure at 13,300 psig on low and high void material.

Table 2 Properties of welds of completed titanium 721 alloy cylinder

Properties	Welds Sub-assy 1 Shop	Welds Sub-assy 1 Lab	Welds Sub-assy 2 Shop	Welds Sub-assy 2 Lab	Base plate
Yield strength, ksi	105.7	106.3	106.0	104.1	109.0
Tensile strength, ksi	121.8	122.1	118.0	118.7	121.0
Elongation, %	9.4	8.3	8.5	10.7	14.0
Reduction in area, %	23.6	19.0	22.8	26.8	24.0
Bend angle, °4T radius	180[a]	180[a]	180[a]	180	180
Charpy V-notch energy Ft lb @ −80°F	25	31	29	35	30

[a] Three of four specimens.

Two $5\frac{1}{2}$-in. thick by 32-in. in diameter hatch forgings and two $5\frac{1}{2}$-in. × 37-in. o.d. by $18\frac{1}{2}$-in. i.d. hatch insert forgings of the Ti 621-0.8Mo alloy were successfully produced. These forgings, along with eight closed impression die forgings, to be used as window inserts (which also have been successfully produced), will be fabricated into two 7-ft diam hulls.

Weld wire certification tests have been completed (Aug. 13, 1970), and authorization to use the wire for welder certification and weld procedure qualification has been issued. Results of tests on filler wire certification weldments are shown in Table 3.

High Strength Plastics

Filamentary composites have excited the imagination of both the aerospace and hydrospace industry. Data on four well-known filaments are shown in Table 4. Of these filaments, glass is the one on which the hydrospace industry has concentrated its attention. An examination of Fig. 14 will show a series of general relationships for glass reinforced filamentary composites. First, the linear relationship between interlaminar shear and compressive strength can be seen on the two vertical ordinates. That is to say, as the interlaminar shear strength goes up, the compressive strength increases accordingly. Further, it is seen that increasing resin yield strength results in increasing compressive strength of the composite. Presently, we are confined to resins in the 20,000 psi compressive strength range. New resins being produced experimentally by the Union Carbide Co. and by Navy laboratories are yielding resins with compressive strengths in the 30,000 psi range and have resulted in composites of increased strength, as shown in curve 2. Finally, by improving the quality of the bond between the filament and the resin we can focus our attention on Curve 1 with compressive strength improved even further. In summary, higher compressive strength filament wound plastics can be

Table 3 Properties of filler wire certification weldments

	Avg value	Spec. req., min
DTT, ft @ 30°F	1800	1000
Tensile yield 0.2% 05, ksi	113.0	100
UTS, ksi	128.5	118
Elong % in 4D, 1 in.	13.0	10.0
Reduction in area, %	29.4	20.0
Charpy V @ −80°F	32.0	20.0
ft @ +32°F	39.7	25.0

Table 4 Comparison of properties of filaments for filament wound plastics

	Properties		
Filament material	Density, lb/in.^{3}	Tensile strength, psi	Tensile modulus, psi $\times 10^{-6}$
"S" glass	0.090	700,000	12
Boron	0.090	300,000	60
Graphite (Th-25)	0.054	200,000	25
Graphite (Th-50)	0.054	400,000	50

expected with 1) improvement in filament strength, 2) increases in resin matrix compressive strength, and 3) improved filament to resin matrix bonding.

Despite rapidly moving developments leading towards the achievement of higher strength plastics, we are still faced with a major limitation imposed by difficulties in fabrication. The fabrication of a serviceable vehicle will still require hatches, sections of differing thicknesses, joints, bonds between structural elements and guarantees of quality—none of which are yet readily achievable. One of the factors, for example, which influences the strength of a glass-plastic composite, is the void content. Fig. 15 shows a comparison of properties of a material of a low void content and one of high void content after exposure at 13,300 psi hydrostatic pressure for 3 months. The degradation in the compressive strength and the increased water absorption speak for themselves. Fortunately, ultrasonic techniques have been developed which permit the direct nondestructive measurement of void content ultrasonically and, as a result of Navy research, a technique for nondestructively assessing interlaminar shear; and hence, compressive strength by ultrasonic measurements has been established and is shown in Fig. 16.

Buoyancy Materials Utilization in Hydrospace

Conventional syntactic foam buoyancy materials are based on a filler of low density, hollow glass microspheres, 10–90 μ in diameter, embedded in an epoxy resin. These conventional syntactic foams have an average density of 42 p.c.f. and a glass packing fraction of approximately 65% by volume. The latest information on syntactic foam formulations indicates that the 42 p.c.f. nominal density foam will withstand hydrostatic compressive pressures of 20,000 psi, whereas a 38 p.c.f. density foam will withstand somewhat lower pressures. Both Navy-developed formulations and commercial formulations of syntactic foam are available to adequately perform as deep submergence buoyancy materials.

New classes of syntactic foam buoyancy materials are now under study. Their attainment will largely depend upon the successful development of low-density, hollow glass minispheres, 300–350 μ in diameter. These minispheres, when combined in a binary mixture with 10–90 μ size microspheres and embedded in an epoxy resin, will result in a syntactic foam buoyancy material with a maximum density of 34 p.c.f. and a glass packing fraction as high as 80% by volume. Of the interesting possibilities with a syntactic foam, we may speculate on the likelihood of formulating such a foam with a bulk modulus equal to that of water. An examination of Fig. 17 will show that syntactic foam is similar in bulk modulus or compressibility to water. It is evident that if we are able to tailor such a buoyancy material with a compressibility equal to that of water, we will have eliminated a source of troublesome vehicle trim problems for the designer.

The second approach is the incorporation of large (3–10 in., diam) hollow spheres, probably of glass, in the previously described syntactic foam. By utilizing glass spheres of various diameters in close-packed arrangement, buoyancy materials of less than 28 p.c.f. can be obtained. These buoyancy systems may be subject to sympathetic implosion of the glass spheres, however, and must be carefully investigated.

Several candidate sphere materials exist from which these modules may be produced. The nomograph, Fig. 18, compares candidate sphere materials and highlights the favorable properties of glass and the even more desirable properties of beryllia and alumina. At some time in the future it is expected that spheres of alumina will be available. The present availability of massive glass and the large amount of information which we now possess on this material make it a good candidate for buoyancy applications.

Upon the development of additional successful structural response information, massive glass may become a major contender for large pressure hulls, eventually leading to manned pressure hull application.

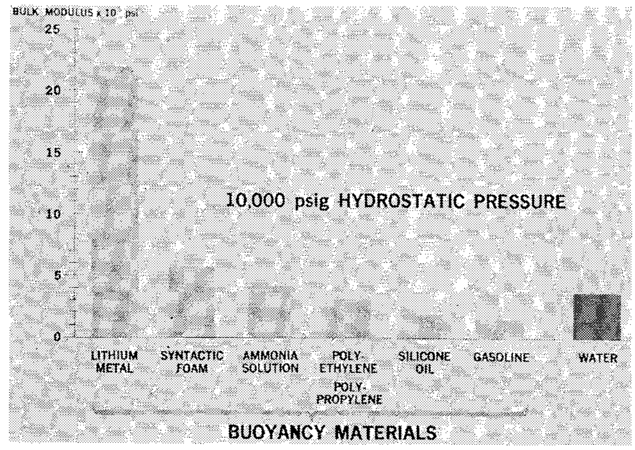

Fig. 17 Bulk moduli of buoyancy materials.

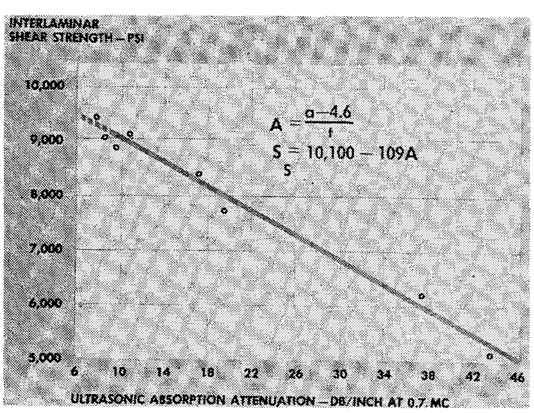

Fig. 16 Relationship between interlaminar shear strength and ultrasonic measurements for filament wound plastics.

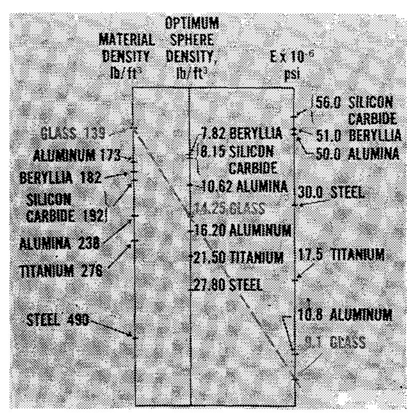

Fig. 18 Nomograph showing candidate sphere materials for use in buoyancy materials, for design pressure of 13,500 psi.

Encapsulants and Coatings Utilization in Hydrospace

A myriad of problems is to be expected in this area. Coatings for vehicles, gaskets for hatches and sheathing for cables are only a few of the applications which will require the careful selection of existing materials or the development of new resins and compounds. Plastics and elastomers with special properties will be needed to solve many of these problems. A typical problem on which we are working involves the encapsulation of stator windings in a free flooding submersible motor. Successful encapsulation will lead to the development of such free flooding motors for use external to the pressure hull at deep ocean pressures.

In another area of encapsulating materials, the Navy has developed butyl formulations with low water permeability for application as hydrophone boots. Permeabilities as low as 8×10^{-10} g water/cm^2/hr/mm Hg were realized. This was significantly better than other materials such as neoprenes, which are 40 times more permeable; natural rubber, 75 times more permeable; and polyurethanes, 300 times more permeable than the butyl materials. An interesting and unexpected discovery resulting from this work has been the fact that this butyl rubber boot material was found to be considerably less permeable at high hydrostatic pressures than at ambient pressures. The reason for these somewhat unexpected results are discussed from a thermodynamic point of view in Ref. 1.

Materials science will be called upon to marshall all its resources and ingenuity to keep pace with the growing demands of ocean engineering and may very well be, in the final analysis, the key to effective use of the sea.

Reference

[1] Lebovits, A., "Effect of High Hydrostatic Pressure on the Permeability of Elastomers to Water," *Rubber Chemistry and Technology*, Vol. 39, Sept. 1966, pp. 1298–1307.