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HIGH PRESSURE - HIGH TEMPERATURE RESEARCH AND NEW ELECTRONIC MATERIALS

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Introduction

Because of the diverse nature and accelerated pace of work currently going on in this field, the title may indicate conditions ranging from a few hundred atmospheres of pressure to several hundred thousand, and temperatures from several hundred degrees to several thousands. Pressure-transmitting media also may differ, being either gaseous, liquid or solid, and therefore, of variable degree of hydrostaticity.

To alleviate the problem with respect to intensity conditions at the USASRDL, we have adopted a classification system based on environmental intensity. It is presented in Table I.

Table I

Classification of Pressure-Temperature Intensities

Descriptive terminology	Pressure range in atmospheres	Temperature range in Deg. Kelvin
Low	below 3×10^2	below 3×10^2
Moderate	3×10^2 to 3×10^3	3×10^2 to 3×10^3
High	3×10^3 to 3×10^4	3×10^3 to 3×10^4
Very High	3×10^4 to 3×10^5	3×10^4 to 3×10^5
Ultra High	beyond 3×10^5	beyond 3×10^5

This article will deal primarily with work at pressures above 30,000 atmospheres, temperatures up to 3×10^3 deg Kelvin, and the use of solid pressure-transmitting media.

Instrumentation

Current chemical processes requiring pressure generally are carried out below 3×10^2 atmospheres, using fluid pressure-transmitting media. Autoclave type of vessels are commonly used. The investigation of mineralogical and chemical systems are frequently carried out in bomb type of apparatuses to pressures of approximately 3×10^3 atmospheres. Gases or vapors are used as pressure media. Various physical researches have been carried out to 3×10^4 atmospheres with fluid media by means of piston-cylinder chambers using Bridgman seals(1), and also by means of shock systems. Where heat is required in addition to pressure, either internal or external sources can be employed such as electrical resistance heaters, or, in some cases, steam or heat resulting from exothermic chemical reactions.

Beyond approximately 3×10^4 atmospheres, all usable fluid media solidify. Upon solidification, these materials become brittle and possess relatively high shear strengths. In most cases, therefore, they no longer are capable of transmitting pressure with a sufficient degree of homogeneity. In order to approach a hydrostatic transmission of stress above 3×10^4 atmospheres, it has been necessary to make use of solids that are weak, or so to speak, soft, under pressure. Another method of description is that they must possess a low internal friction, that is, a low shear strength while under pressure above 3×10^4 atmospheres.

Several elements, compounds and aggregate materials are now known which work with a remarkable degree of efficiency in this very high pressure range. Some of the more common are listed in Table II.

Table II

Several Solid Pressure-Transmitting Media

Elements	Compounds		Aggregates
Pb	AgCl	$CuCl_2$	hot pressed BN
	AgCN	HgCl	lithographic limestone
	AgBr	Hg_2SO_4	soapstone
	Ag_2SO_4	NaCl	pyrophyllite
In	$CaCO_3$	NH_4ClO_4	
	$CoCl_3$	PbO	
	CuCl	$PbSO_4$	
	$PbCO_3$		

Most of these media possess relative shear strengths less than 5 per cent up to pressures of 5×10^4 atmospheres(2). Where electrical circuitry or elevated temperatures are to be used, electrical and thermal conductivity, in addition to physical and chemical stability must be, of course, taken under consideration.

Mention also should be made of the hysteretic transmission of pressure observed when solid materials are used. A variation of transmitted response between the application and removal of force may vary from 10 per cent to as high as 100 per cent in some cases. This phenomenon is due to a combination of external and internal friction within the solid media and between the latter and pressure chamber components. This effect can be reasonably controlled, however, and to some extent advantageously manipulated, by the use of dry lubricant or frictional powders such as MoS_2 and Fe_2O_3, respectively. The latter type of materials also are effective in reducing leakage of solid media through machine tolerances of chamber components.

Pressure vessel designs which have been developed by workers and currently used above 3 x 10^4 atmospheres fall into two main catagories*; namely, variations on the piston-cylinder principle, and that of converging multiple pistons. Three basic patterns of pistons currently in use are: 1) the simple, or right circular cylindrical piston; 2) the tapered or anvil type of piston; and 3) the stepped, or compounded piston.

Two basic types of retaining cylinders are commonly used: one is the multiple series of concentric right circular steel rings with either a steel, carbide or ceramic inner bore cylinder, the other is the multiple series of concentric tapered steel rings with a similar choice of inner bore material. Lateral support to the normal strength of the materials is developed either by thermal interference fitting of the oversize inner rings within outer rings as in the first mentioned design, or by mechanical interference fitting as in the latter type. The mechanical fit, although more difficult to fabricate, is capable of much greater support. In addition, techniques such as multistaging, double-acting cylinder assemblies, and peripheral piston support have been used to further strengthen cylinder assemblies. Six types of apparatus designs are shown in Fig. 1. A brief description of each follows:

The Bridgman anvil apparatus (3) is simple in design but extremely effective. It can be used successfully to pressures of 1 x 10^5 atmospheres at room temperature. Two opposed tapered carbide pistons with flat opposing work faces are given lateral support by shrunk-on hard steel rings. Force is applied to the back surfaces of the pistons by means of a hydraulic press. The sample used in the apparatus is a thin disk approximately 0.025 cm thick. The attainable pressure of 10^5 atmospheres is about twice the normal crushing strength of the piston carbide. This gain is possible because of the lateral support of the steel sleeve plus the fact that loading is done only on a small portion of the compression member. This allows the surrounding piston material, which is stressed to a lesser degree, to absorb part of the load. Because of the absence of any cylinder wall for lateral constraint, this type of apparatus is restricted to very small specimen volumes, with little possibility of incorporating an internal heating device. The effectiveness of this design, therefore, is essentially limited to physical studies at room temperature.

Griggs and Kennedy (4) have used an adaptation of the Bridgman anvil with the addition of an external furnace. Their design has been used to investigate mineral and chemical systems. Elevated temperatures tend to weaken the components of the apparatus, however, and at 800K the maximum attainable pressure is 8 x 10^4 atmospheres. At a temperature of approximately 1300K, the capability drops to approximately 2 x 10^4 atmospheres. This attrition of strength with elevated temperature emphasizes the advantages of a well-insulated, compact internal heating device. The reaction volume of this apparatus has the same limitation as that of Bridgman.

Drickamer (5) by completely enclosing the anvils, has extended the pressure range to beyond 2 x 10^5 atmospheres. NaCl is used both as a pressure-transmitting medium and for optical observation windows (indicated by cross-hatched area). Dynamic optical studies to very high pressures are possible with this ingenuous design. By having the entire tapered face of the anvils bear on the pressure medium, additional support is given to the piston material. More gradual stress gradients also are realized. Drickamer has stated that for a sample pressure of 2 x 10^5 atmospheres, the average stress across the piston face is but 5.3 x 10^4 atmospheres. A gain of almost 4 to 1. As in the previous two designs, the specimen volume is very small.

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* No consideration can be made here of the General Electric "Belt" apparatus since this still remains a closely guarded secret.