HIGH PRESSURE PROCESS FOR IMPROVING THE MECHANICAL PROPERTIES OF METALS

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FIG. 1

FIG. 2

FIG. 3

FIG. 4

COMPARATIVE CREEP TEST PLOTS

UNTREATED SPECIMENS

HIGH HYDROSTATIC PRESSURE TREATED SPECIMENS

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This invention relates to processes involving very high hydrostatic pressure, and products treated by the application of such pressures. In experiments involving high pressures in the order of 1,000 to 50,000 atmospheres and higher, many apparatus have been used. One such apparatus involving a hydraulic piston arrangement is disclosed in my copending patent application Serial No. 619,942, now abandoned, filed June 12, 1959. Any such apparatus normally has an upper pressure limit; and this pressure limit is often lower than might be desired.

Accordingly, one object of the invention is to increase the pressure which may be obtained with conventional hydrostatic pressure apparatus.

This object is achieved, in accordance with one aspect of the present invention through the use of a supplemental layer of material over the inner sample material to be compressed, where the supplemental layer is of a solid, non-elastomeric material having the property that it is reduced in volume with increasing pressure more rapidly than the sample which is to be pressurized. In certain cases, the reduction in volume of the outer layer is accompanied by an abrupt densification, which is particularly helpful in the intensification of the pressure on the inner sample.

In accordance with one feature of the invention, therefore, the pressure on an article can be intensified by encasing the article in material which decreases in volume more rapidly than the article, with increasing pressure, and then subjecting the encased article to elevated pressure. In accordance with a preferred embodiment of the invention, the outer casing may be of a material, such as bismuth or bismuth containing alloys, which is subject to abrupt densification at high pressures.

With regard to another phase of this invention, it has been found that the application of high pressure to certain substances produces unexpected and permanent changes in the properties of these substances. Thus, when test specimens of high purity iron were encased in a bismuth-containing jacket and the assembly was held at a pressure of many thousands of atmospheres for a week, many properties of the iron were permanently altered. Thus, for example, the creep resistance and hardness of the iron was greatly increased; other properties of the iron were also changed as set forth in detail below.

Now, it is believed that the effect of the high pressure is to increase the number, location and arrangement of dislocations in the crystalline structure of the iron. "Dislocations" are defects in crystalline material and are described in detail in a book entitled "Dislocations and Plastic Flow in Crystals" by A. H. Cotrell, Oxford, Clarendon Press, 1953. According to theory, the number and form of dislocations affects some properties of materials such as hardness, creep resistance, and electrical conductivity, but does not affect certain other properties, such as the modulus of elasticity, for example, to any great extent. Following the high pressure treatment as described above, the samples were found to have permanently improved hardness and creep resistance. Other observable factors also indicated that the number and location of dislocations in the material have been greatly altered.

In accordance with another feature of the invention, therefore, crystalline material is subjected to high pressure to produce alteration in the number and location of dislocations in the material and significantly change a group of properties of the materials which are dependent on dislocations, and force is thereafter applied to the material to utilize the properties which have been changed. For example, the pressure-treated element may be used as a wear-resistant surface, as a structural element, or as a magnetic or electrical component, in systems where the properties provided by alterations of dislocations are desirable.

For crystalline materials, time and hydrostatic pressure levels exist, above which appreciable permanent changes in the properties of the materials occur. It is to be understood that this phase of the present invention does not involve deformation of the materials as by macroscopic stresses other than hydrostatic, nor does it involve changes in the gross crystal structure of materials such as the transformation of graphite or other forms of carbon to diamonds. Instead, it encompasses only permanent changes other than those specified above in solid crystalline materials produced by hydrostatic forces. For each material, the threshold at which significant permanent changes in the properties of the pressure-treated material occur will be designated the "dislocation alteration threshold." When the pressures and time periods are in this range, the state of dislocations including their number, shape, location, type of aggregation, movement, entrapment, formation and interlinkages, are altered. This threshold is characterized by the increase in creep resistance by more than ten percent, or by an increase in indentation hardness number of about three points or more, as these criteria are defined hereinafter.

In accordance with another aspect of the invention, therefore, the present invention contemplates subjecting a solid crystalline material to a high pressure beyond the dislocation alteration threshold, and assembling the material into a device in which the permanently altered properties of the material improve the operation of the device. It is also to be noted that the components are preferably fabricated to the proper shape prior to pressure treatment.

In accordance with additional features of the invention, the wearing surfaces of an apparatus may be provided with hydrostatically pressure-hardened components. One example of the use of such components is the wearing surfaces of the nozzles in synthetic fiber-extruding devices such as spinnerettes. Hydrostatically pressure-hardened conducting material may also be employed as electrical contact elements. Semiconductors and magnetic cores may also be treated to change their electrical properties. Other objects, features and advantages of the invention will become apparent from a consideration of the following detailed description, from the claims, and from the drawings in which:

FIG. 1 is a diagram useful in explaining the effect of high pressures;

FIG. 2 is a cross-sectional view of a sphere of one material encased in a shell of a different material;
FIG. 3 represents a test sample encased in a jacket which undergoes a volume shrinkage at high pressures, in accordance with the invention.

FIG. 4 is a chart showing comparative creep test results for untreated and pressure-treated specimens.

FIG. 5 shows a simple electrical circuit diagram employing a pressure-treated magnetic core, in accordance with the invention.

FIG. 6 represents a circuit including a vacuum tube having a semiconductor source of electrons which has been pressure-treated, in accordance with the invention.

FIG. 7 shows a switch in which the contacts have been pressure treated, in accordance with the invention; and

FIG. 8 represents a spinnerette in which the spinning nozzles have been hardened pursuant to the principles of this invention.

Before considering the drawings in detail, it is appropriate to define the term “compressibility,” which is important in the consideration of the present invention. The compressibility of a material is a measure of its ability to be reduced in volume as increased pressure is applied. Thus, the following equation defines the compressibility k:

$$k = \frac{dV}{(dP)V}$$

where k is the compressibility for a given range of pressure.

is the change in volume per unit volume, and dP is the change in pressure. The minus sign indicates a decrease in volume as pressure is increased.

With this notation, it may be noted that materials which are more compressible than others will have a higher compressibility than the other materials.

With reference to FIG. 1, it is assumed that the circle 12 represents a homogeneous sphere of crystalline material. In this connection, the word “crystalline” is defined as “having atoms arranged in a fairly regular pattern or lattice.” Polymeric materials are included as crystalline because of a type of regularity of molecular structure possessed by them. The radius of the sphere 12 at atmospheric pressure is indicated by r₁. When a high pressure, in the order of thousands of atmospheres, is applied to the sphere 12, the radius r₁ is reduced to another radius indicated in FIG. 1 by the radius r₂. Another radius r₃ within the sphere 12 is similarly reduced to a smaller radius r₄.

FIG. 2 is a cross-sectional view of another sphere in which the outer shell 14 is of the same material as that shown in FIG. 1, and wherein the central core member 16 has a smaller compressibility, or is less compressible than the outer shell 14. The radius r₅ of the outer shell 14 is reduced to the radius r₆ upon the application of high hydrostatic pressure. The change from radius r₅ to radius r₆ will be less than the shift from radius r₁ to radius r₂, in the case of the isotropic sphere of FIG. 1. In the case of the radius r₅ however, which is approximately equal to r₂ under atmospheric pressure conditions, it is reduced to r₆ when high pressure is applied to the assembly of FIG. 2. Because the material 16 is less compressible than the outer material of sphere 12 of FIG. 1, the radius r₅ is greater than the radius r₂.

In the case of a homogeneous sphere such as that shown in FIG. 1, the pressure throughout the sphere is generally accepted to be equal to the pressure applied to the outer surface of the sphere. In FIG. 2, if the inner sphere 16 were not present, the inner radius r₇ of the shell 14 would be reduced to the radius r₈ as indicated in FIG. 1. Accordingly, to maintain the inner wall of shell 14 at a larger radius r₈, additional pressure must be exerted at the interface between sphere 16 and shell 14. It is clear, therefore, that the inner sphere 16 is subjected to a pressure which is greater than that which is applied to the exterior surface of the entire assembly of FIG. 2.

As a general principle, it can therefore be stated that an increase in pressure may be obtained by encasing a specimen having a given compressibility in a jacket of larger compressibility. Under these conditions, the outer, more compressible material will exert additional force on the inner core member, thus subjecting it to higher pressures than are applied to the entire core and jacket assembly.

Instead of employing material which merely has a larger compressibility as a jacket, materials which undergo an abrupt densification or reduction in volume under pressure may be employed. Such a property may be found in combination with a material having a higher compressibility than the encased material. Many materials are known which have such abrupt reductions in volume, and in some cases they are a result of a polymeric transformation from one crystal structure to another closer-packed type of crystal structure. In other cases, it is believed that an outer electron shifts to an inner electron shell which is closer to the atomic nucleus; and in still other cases, abrupt densification occurs under circumstances which are not completely understood. In Table I set forth below, the pressure levels at which abrupt transformations take place for four elements are set forth.

<table>
<thead>
<tr>
<th>Element</th>
<th>P. atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium</td>
<td>7,600</td>
</tr>
<tr>
<td>Bismuth</td>
<td>25,000</td>
</tr>
<tr>
<td>Barium</td>
<td>60,000</td>
</tr>
<tr>
<td>Antimony</td>
<td>85,000</td>
</tr>
</tbody>
</table>

The changes in volume are relatively large, with that for bismuth being about 9 percent, and that for barium being about 2 percent. The jackets need not be in the form of pure chemical elements, thus, Percy W. Bridgman in the Proceedings of the American Academy of Arts and Sciences, volume 82, pages 101 to 156, 1953, discussed a range of bismuth-tin alloys which densify abruptly at about 25,000 atmospheres.

As an example of the application of the principles set forth above, FIG. 3 shows a ¼ inch diameter test sample 18 which is encased in a jacket 20 of at least ¼ inch diameter of a metal alloy which has an abrupt densification with increasing pressure in a test section of standard form and is described in detail on page 88 of the Metals Handbook of the American Society for Metals, 1948 edition. Four test specimens as shown at 18 in FIG. 3 were carefully machined with attention given to avoid overheating and excessive straining. The specimens were formed from vacuum-melted and simultaneously vacuum-cast iron. They were stress-relieved for one hour at 1800°F, furnace cooled at a rate of 150°F per hour to 1000°F, and then air cooled to room temperature. A chemical analysis indicated impurities of less than 0.003 percent total carbon by weight, 0.015 percent oxygen by weight, 0.0018 percent nitrogen by weight, and the remaining impurities less than 0.01 percent.

The jacket 20 on each of the four samples was composed of a material weighing 430°F, just below the temperature of boiling water. The alloy included 16 percent tin, 32 percent lead, and 52 percent bismuth by weight. Of the four specimens, two were subjected to a high hydrostatic pressure of about 28,000 to 35,000 atmospheres in a pressure apparatus of a known type. The alloy jacket is more easily compressible than the iron by a factor of about five. At pressures of above 25,000 atmospheres, the alloy jacket abruptly densifies, enhancing pressure on the specimen in the manner described above.

Two of the specimens were successively subjected to
these high pressures for about a week. After the pressure treatment, the jackets were melted from both the two pressure-treated specimens and the two unpressurized specimens. The four specimens were then stored for six months in order to minimize effects of a temporary nature, which might otherwise have affected subsequent tests.

Creep tests were then performed in creep machines of a known type at a temperature of 800°F. and at a stress of 1000 lbs. per square inch. The results of these tests were indicated in Table II and in Fig. 4:

### Table II

<table>
<thead>
<tr>
<th>Spec.</th>
<th>In/In. Yield Strain</th>
<th>Hr-1</th>
<th>Min. Creep Rate</th>
<th>Hr-1</th>
<th>Rupture Time</th>
<th>Last strain Measurement (at Life Shown), Inches per Inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0002</td>
<td>0.0007</td>
<td>2254</td>
<td>.25 at 813 hrs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.0003</td>
<td>0.0008</td>
<td>906</td>
<td>.13 at 88 hrs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.0004</td>
<td>0.0009</td>
<td>6335</td>
<td>.26 at 566 hrs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.00048</td>
<td>0.0011</td>
<td>1.029</td>
<td>.06 at 893 hrs.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Note—Strain measurement is lower for D because extensions were removed well before rupture.

**Creep, In/In.**

<table>
<thead>
<tr>
<th>Hrs.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>.069</td>
<td>.058</td>
<td>.028</td>
<td>.021</td>
</tr>
<tr>
<td>30</td>
<td>.046</td>
<td>.037</td>
<td>.026</td>
<td>.027</td>
</tr>
<tr>
<td>60</td>
<td>.038</td>
<td>.029</td>
<td>.025</td>
<td>.026</td>
</tr>
<tr>
<td>100</td>
<td>.021</td>
<td>.017</td>
<td>.017</td>
<td>.020</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>.008</td>
<td>.008</td>
<td>.008</td>
</tr>
</tbody>
</table>

Specimens A, B, untreated; C, D, pressurised.

In reviewing Table II and Fig. 4, it should be noted that samples C and D were the pressure-treated samples, and samples A and B were the untreated samples. In brief, it may be noted that the yield strain or extension at elevated temperature was decreased, the amount of transient and the rate of the steady-state creep was greatly decreased, and that rupture-life was increased.

As mentioned above, the mechanical strength at elevated temperatures is increased significantly. Whereas the mechanical strength of certain untreated materials is greatly reduced even at the boiling point of water (100°C; 212°F.), the pressure-treated materials show high mechanical strength at these lower temperatures and even beyond the 800°F. level at which the creep tests were conducted.

With reference to Fig. 4, the very slow elongation of the two pressure-treated samples to the right of the chart is in sharp contrast with the rapid increase in length of the untreated specimens. It is to be noted that the creep curves of Fig. 4 were not carried to rupture; however, all specimens ruptured subsequently as given by Table II.

Hardness tests conducted on ends cut from the specimens prior to the creep tests, showed an increase in hardness from 81.5 to 140 DPH in accordance with the Diamond Pyramid Hardness system of hardness testing. This corresponds approximately to a Brinnell hardness change of from 76 to 135.

There was essentially no change in dimensions of the specimen caused by the pressurizing process. A small increase in the nominal diameter of the test sections (in the order of one percent), appeared to be caused by relative movement of grains past each other, yielding a slightly roughened surface.

In summary, the process in accordance with the present invention enhances mechanical properties of metals such as creep resistance. In addition, it alters the physical properties of solid crystalline material. Another advantage is that no dies are required to maintain shape. Thus, components may be fabricated in a relatively soft condition, and may subsequently be pressure hardened without alteration of size or shape. Furthermore, a number of materials such as relatively pure iron which cannot be hardened by heat treatment alone, are hardened by the present process.

As discussed above, the prolonged application of hydrostatic pressure beyond the dislocation alteration threshold produces permanent defect structure changes in crystalline materials. The pressure applied to the two iron samples C and D was well beyond this threshold. Thus, the dislocation alteration threshold requires an increase in the creep resistance by about 10 percent or an increase in hardness number of about three points, as noted below.

One criterion of creep resistance is the slope of a plot of longitudinal strain versus time as indicated in Fig. 4. The pressure-treated specimens C and D had minimum creep rates of 3 hundred thousands and 2 hundred thousands of an inch per inch, per hour, respectively. The untreated specimens had creep rates of 75 and 93 hundred thousands of an inch per inch, per hour, respectively. Thus, the pressure-treated specimens were from 10 to 50 times more creep resistant than the untreated specimens.

Another criterion of strength at high temperature is stress rupture life given in Table II as "rupture time." The pressure treated specimens had lives which were from three to eleven times greater than the untreated specimens.

With regard to hardness, it has been noted that the DPH hardness increased from 81.5 to 140, corresponding to a Brinnell hardness increase of from 76 to 135. This corresponds to an increase in hardness of 57 or 58 points in both of these systems of hardness measurement.

Thus, while the sample showed an increase in creep resistance of 1000 to 5000 percent, and an increase in hardness number of about sixty points, the dislocation alteration threshold is defined as the level at which the creep resistance increases by more than ten percent and the hardness increases by at least three points in either the DPH or Brinnell hardness systems. At this level and beyond, significant improvement in the dislocation dependent properties of crystalline materials may be observed.

Figs. 5 through 8 represent applications for crystalline materials which have been subjected to pressure treatment as described above. In Fig. 5, the magnetic core 22 of a transformer is made of pressure-treated magnetic material. In the circuit of Fig. 5, alternating current signals from the source 24 are coupled to the load 26 by the windings 28, 30, and 32 on the core 22. The increase in dislocations in the core 22 serves to decrease the conductivity of the core material. Accordingly, the loss in the core material as a result of stray induced currents is reduced.

In the circuit diagram of Fig. 6, signals from the source 34 are amplified by the tube 36 and applied to the load 28. The tube 36 may include a plate electrode 40, a grid 42, and a semiconductor body 44 for providing electrons. The semiconductor body 44 may include a p-type portion 46 and an n-type layer 48 forming a p-n junction. A direct current biasing source 50 and an adjustable resistor 52 apply a low biasing voltage across the p-n junction in the semiconductor body 44. As described in application Serial No. 828,997, filed July 23, 1939, a semiconductor body may have its electron emission properties improved by the introduction of dislocations which pass through the p-n junction near the surface of the semiconductive body. Pressure treatment beyond the dislocation alteration threshold serves to introduce such dislocations through the p-n junction, and therefore enhances emission. In addition, it is contemplated that such pressure treatment will enhance the electron emission of other known emitting surfaces.

Fig. 7 represents a circuit in which solid metal contacts 54 and 56 are hardened by pressure treatment beyond the dislocation alteration threshold. As indicated by the previously mentioned hardness data, a large increase in hardness is effected by this technique.

When
highly conductive material is employed, the reduction in conductivity of the relatively thin contact material is not 

harmful. In circuit operation in the way of completeness, the arrangement of FIG. 7 includes a contact mounting arm 58, insulating support members 60 and 62, a source of current 64, and a load 66. The arrow 68 indicates the application of force through any suitable mechanical linkage to the contact mounting arm 58.

The hardness of pressure-treated components makes them suitable for wearing elements. In this regard, they are useful in spinnerettes in which filaments are formed by extrusion at high pressure.

In FIG. 8, a spinnerette assembly is shown which includes the spinning nozzles 70 and 72, the plate 74 in which the nozzles are mounted, and the holder 76 in which the spinnerette plate 74 is mounted. The spinning nozzles may be made of platinum or other know spinnerette materials. Following formation of the individual spinning nozzles 70, 72 into the proper shape as shown in FIG. 8, they are subjected to pressure treatment beyond the dislocation alteration threshold. They are then assembled into the complete spinnerette as shown in FIG. 8. By this technique, the spinning nozzles are machined or otherwise formed prior to pressure treatment when the metal is soft, and, after hardening by pressure treatment, the nozzles are assembled into the completed spinnerettes.

In connection with the materials which may be employed, it was noted that the specimens of FIG. 3 were of substantially pure iron. By way of example, but not of limitation, other specific materials which may be used include other commonly used magnetic materials; silicon and germanium as well as the other known semiconductive materials; silver, copper and other good conductors; and the six platinum group metals, with preference being given to those with less volatile oxides. These materials are to be preferred for the devices of FIGS. 5, 6, 7, and 8, respectively; however, alloys of the listed metals may also be employed, by way of example.

It is to be understood that the above described arrangements are illustrative of the application of the principles of the invention. Numerous other arrangements may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for improving the mechanical properties of metal specimens without substantial dimensional change thereof which comprises the steps of encasing the specimen in a solid non-elastomeric jacket, said jacket having compressibility greater than that of the encased specimen, and subjecting the encased specimen to high hydrostatic pressure between 1,000 and 50,000 atmospheres.

2. The process of claim 1 wherein the jacket is of a material which undergoes abrupt densification at the hydrostatic pressure employed.

3. The process of claim 1 wherein the material treated is of silicon.

4. The process of claim 1 wherein the specimen treated is of a metal selected from the group consisting of iron, germanium, silver, copper and metals of the platinum group.

5. The process of claim 1 wherein the specimen treated is magnetic.

6. The process of claim 2 wherein the jacket is of a material selected from the group consisting of cerium, bismuth, barium, antimony and alloys thereof.

7. The process of claim 4 wherein the specimen is of iron.

8. The process of claim 6 wherein the jacket is an alloy of bismuth, tin and lead.

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