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Subject: Means for Generating Ultra-High Pressures in an Isostatic Press
by Phase Transformation of Suitable Materials

Introduction:

Much valuable work has been done in the investigation of high pressures with
respect to both the means of generation and the effects. Several hitherto
unknown high pressure crystal forms have been discovered, mainly in metals,
which represent denser (more closely packed) configurations.

Most, if not all of the high pressures reported have been generated by dynamic
presses combining one, two, four or six movable pistons, with hard anvil faces,
acting on a core consisting of the sample embedded in a pressure distributing
medium, such as pyrophylite, which also acts as a gasket. This type of arrange-
ment has many desirable as well as undesirable features. Among the desirable
aspects of this technique is the ability to create pressure in a controlled and
fairly predictable way. Also the configurations have been worked out for
relative ease of disassembly with minimum damage, and reassembly for the next
trial or batch.

However, there are two inherent disadvantages to any dynamic press. One is
that the piston, or movable part, must be supported in the direction of thrust
and the load becomes concentrated over smaller cross sections than in a solid
spherical restraint with fluid pressure transmission; therefore, the ultimate
strength of materials can be more easily exceeded. The highest pressures we
could find mentioned in the literature, for a dynamic anvil press was about
500 KG over very small areas, and consequently small volumes. But another
problem with anvil presses is that it is difficult to get an even pressure
distribution across the faces, because of the geometry. Finally, the need
for precise machining of a multitude of parts makes such presses inherently
expensive.

As opposed to the foregoing, it is possible to design a simple static press
in which the "core" or sample holder would be preferably spherical, although
cylindrical should pass. This would contain the sample to be treated, sur-
rounded by a material which becomes fluid (liquid or gas) upon changing state
(melting or vaporizing) with an accompanying significant increase in volume.
Such a "press" has no movable parts; the pressure is self-generating from

within by the application of heat; the pressure transmission is uniform since the medium is fluid; precise machining of parts is minimal by employing suitable semi-rigid envelopes and shims as will be discussed later. One relies on the sheer mass of the supporting solid body to contain the pressure. One difficulty is in calculating the pressure to be obtained without experimentation.

The balance of this discussion will be limited to the use of uranium hexafluoride (UF_6) as the pressure generator. The first section deals with the physical properties of UF_6 as pertaining to pressure generation, and second section with equipment to hold ultra high pressures.

UF_6 is a very interesting, and perhaps unique material in many respects. It has an unusually high vapor pressure as a solid. This reaches one atmosphere at $56°C$, so that in a sense it "boils" before it melts. The melting point is $64°C$ at 1137 mm. mercury or 1.5 atm. The most useful property for our purposes is the large expansion on melting. The ratio of specific volumes of liquid to solid at the melting point is 1.34:1.

Attached is an article "The Chemistry of Uranium", J. J. Katz, E. Rabinowitz - McGraw Hill, 1951, (Exhibit 1) which summarizes most of the published data on this material. The use of the Claperon Equation on page 404 appears to be in error. The change in melting point with pressure ($\frac{dT}{dp}$) shows $0.00505°C$/atm. or the reciprocal of about 200 atm./deg. Also attached is a phase diagram from "Uranium Hexafluoride - etc. - A. deWitt (1960), (Exhibit 2). At the bottom of the diagram is shown a different value, $\frac{dT}{dp}$, namely .0439 deg./atm. = 22.78 atm./deg. My own calculation, using published densities for solid at $1°$ less than melting point and for liquid at $1°$ more, gives the numbers as shown in Exhibit 3, which essentially agrees with (2).

This pressure change with temperature is not very impressive until it is realized that ΔV is based on the specific volumes in a system that permits such an expansion (.278 - .208 = .070 cc/gm). If the system could be made completely rigid and the chamber containing UF_6 completely filled with solid before heating the ΔV in the formula $\frac{dP}{dT} = \frac{\Delta H_f}{T(\Delta V)}$ would be 0, making the pressure infinite. In the real world this will not happen as there will be enough elastic and inelastic give to make the pressure finite. If the capsule is loaded with solid to exactly 74.6% of capacity, there will be enough room for all the material to melt, and the only pressure left is the vapor at the final temperature. At the critical temperature of $249°C$, this is only 44 atm. Between the two extremes (100% filled with solid and 74.6% solid) any pressure desired could be created. It is interesting to note that if there is sufficient pressure, it is possible to increase the melting point curve such that liquid never appears. This was reported by Bridgeman in "Physics of High Pressure" - MacMillan (1931), in which the author reports following the melting point of CO_2 to $93°C$ at 12,000 kg/cm^2, whereas the critical point is $30°C$ at 75 kg/cm^2. Page 207 of that publication is attached as Exhibit (4). Above the critical temperature in a confined chamber the ΔH in the Claperon equation probably should be the heat of sublimation. If the sample is expected to shrink in volume as a result of compressability or change in crystal form the volume ratio of UF_6 to sample should be enough to maintain the desired pressure. The compressibility of liquid UF_6 is not published, but can be ignored because we have a situation equivalent to forcing four gallons into a three-gallon can.

It is impossible to predict what may happen to UF_6 at ultra high pressures, as such work has not been done. It is possible other solid forms of higher density may occur. Any envelope-gasket used in conjunction may change also. Since UF_6 reacts with most materials except saturated fluorides, convenient sample envelopes can be formed of LiF, MgF_2, CaF_2, etc. The first two easily form clear solids at reasonable pressures and are plastic enough to act as gaskets similar to pyrophylite.

Although both Mr. Foulks and the writer have had extensive experience with UF_6 while with the A.E.C., the operating conditions did not exceed 1500 P.S.I. (at least on purpose). One homely observation was made by the writer when a worker made a slight error which illustrates the pressure that is generated when the solid does not have room to melt. A nickel tube with 1/8" I.D. and 3/8" O.D. [⊙ cross section] and eight inches long had become plugged at one end where there was a pressure fitting. The other end was open to a supply of liquid UF_6 at 1500 P.S.I. and about 287°C. Standard procedure to change a fitting was to freeze off the eight inch nipple with dry ice, starting at the outer fitting and working back to the supply. This made about a 7" plug of solid UF_6 so that the fitting end could safely be opened and changed. After doing so, flow was restored by flaming the end connected to the supply and working it back toward the fitting. The worker was careless and flamed the middle first, causing a 2"-3" section of UF_6 to be able to melt with a plug still on each end. The heavy walled tube "gave" enough to cause a swelling about corresponding to one-third of the volume inside, but did not fracture, as the "big push" was over and it was strong enough to contain the gas pressure of the liquid. If the nickel has been less ductile it would have split open.

Let us now proceed to equipment which will not "give" enough to dissipate the pressure built up while solid is trying to melt. We present two concepts, one by the writer which is not at all suited to more than one trial. It would be resorted to only in cases of extreme pressure, and when time of forming it is not important. Time becomes a factor because it consists of an electro-formed sphere of large area. Plating solutions are limited in current carrying capacity, especially at lower temperatures which are necessary to keep from generating too much pressure in the core. A diagram of the core and the entire assembly is attached in Drawing #1.

Without belaboring the details of how, let me simply state that the sample can be easily embedded in a LiF sphere. This can be placed in an electro-formed nickel sphere (with spacers to center it). The void between the LiF and nickel is filled by sublimation with UF_6 solid to an amount dependent on the approximate ultimate pressure desired. The inlet tube is sealed in a manner such that further electroforming will bridge over the seal. This core is safe at ambient temperatures.

The above described core is then plated for the first inch in a commercial "Perflow" solution, which is a standard "Watts" coumarin addition agent. This produces a very ductile deposit which has a leveling effect. More metal is deposited in depressions or low current density areas and enables one to smooth out lumps from interior seals, etc. For the next two inches I would recommend taking advantage of the added strength of laminates with the high surface area/volume ratio. This can be accomplished by removing the object from the plating solution dipping in chromic acid, spray washing, and resuming the plating. The resulting coat could actually be stripped off if the surface

were cut, so that it is a discrete surface. I would recommend at least one
hundred layers per inch in spite of the inconvenience. Beyond this lamellar
region I would use a plain nickel fluoborate solution with buffering agent.
This has at least twice the current carrying ability of a "watts" bath. This
would be interrupted about once per inch with a nominal coating of copper in
order to interrupt any incipient flaws from continuing and help absorb and
equalize stress formations.

Uniform plating over the entire surface can be accomplished by surrounding it
with equidistant anodes in one plane and rotating it in the other plane with
belt driven plastic rollers. Electrical contact is made with a graphite brush
or a shallow hard rubber cup with a pool of mercury which is contacted with
insulated wire through the bottom. This would conform to the changing diameter
of the sphere. No specific size is shown since this will depend on the pressure
expected. No provision has been made for interior heating, nor monitoring
pressure since it is expected that this setup would be used only at pressures
that I would not know how to measure directly, and at temperatures not too
much above the melting point so that heating the whole globe is practical. In
other words the UF_6 capsule would be nearly filled. Since nickel is now \$2.70/
lb. for large forms the outer layers can be switched to a 30% iron alloy, which
is a fairly new development, but there is no information about relative strength.

Needless to say, this has to be considered a disposable container as it will
need a "diamet" saw to open it unless it opens itself. However, you will notice
that no special tools, machining or materials are involved. Second hand plating
equipment is always available. Occasionally there might be a reliable job shop
with open time for a special project, but I tend to shy away from this alterna-
tive. As a matter of fact I know where the necessary equipment can be had for
the taking. The main expense other than plating tanks and a motor-generator,
is the cost of nickel and time, which for the moment is nominal. Assuming the
sphere were two feet in diameter this would be approximately 2,335 pounds of
nickel at \$2.70/lb. = \$6300. Current needed would be 969 Kw. hours @ \$0.3
(nominal) = \$29 and one month's time. A space for equipment and installation
depends on what arrangement is available at the time. A very small vacant gas
station is about the right size.

Drawing No. 2 shows Mr. Foulks suggested assembly. This is schematic and is
not intended to show every refinement of detail. It is much to be preferred
because of the fact that it is suited to reuse. Provision is made for certain
parts to be expendable, but these are not expensive. Because it is not a solid
mass, it will not be quite as fool proof as to leaks of vapor, but we feel it
can be made good enough to hold nearly any pressure that the sphere will. Be-
cause of the need to machine the large intersecting blocks to close tolerances,
and since we can not do this ourselves, it is expected to be more expensive.
On the other hand very little space is needed since the assembly itself is only
a few cubic feet and the plating tanks are not needed. Fabrication time would
depend on someone's shop schedule. His comments are attached on the drawing.

Enclosed separately is a discussion of a specific application for use of this
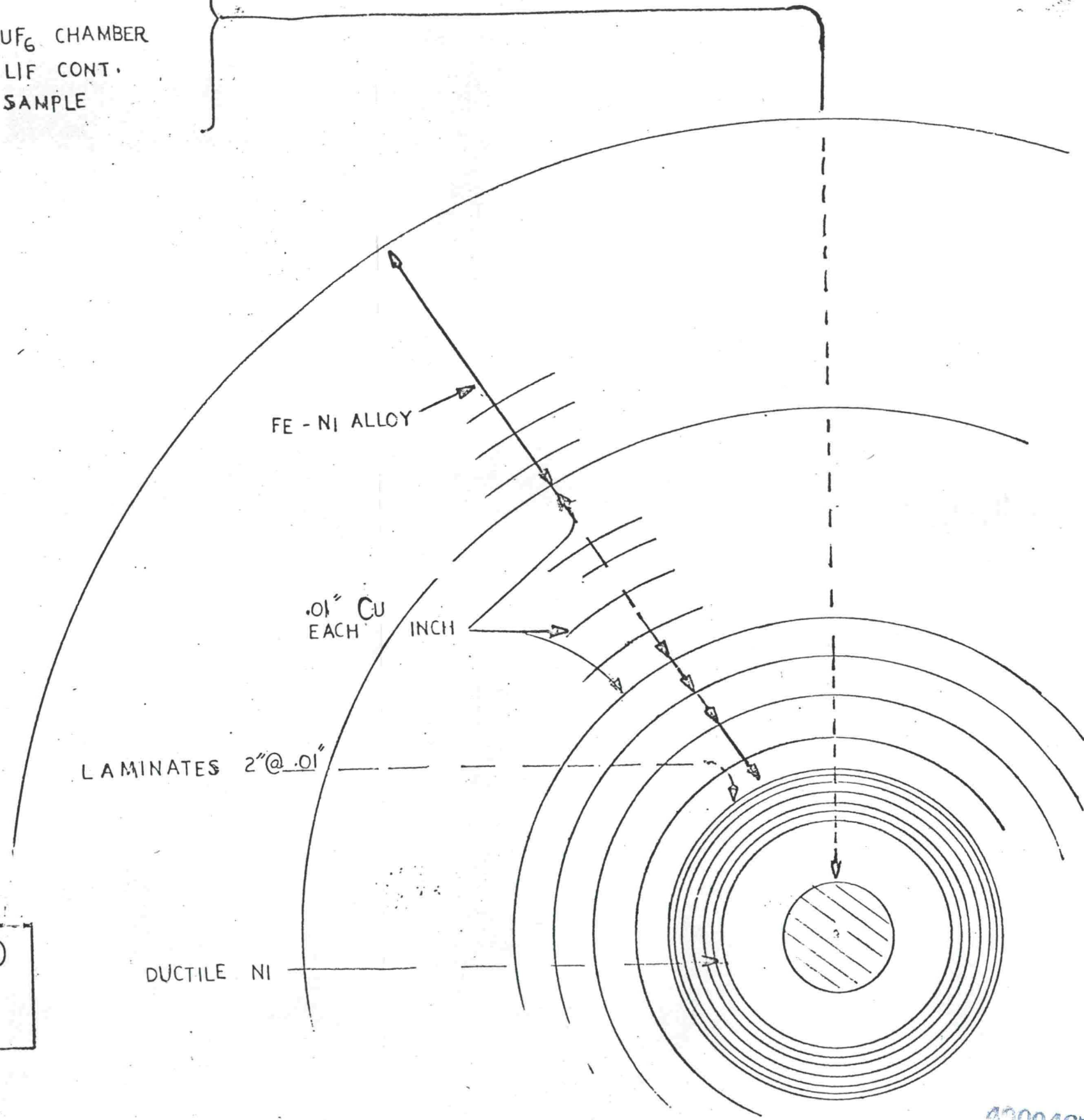equipment.

William A. Harshaw, II

William S. Foulks, Jr.

DETAIL OF CORE
(NOT TO SCALE)
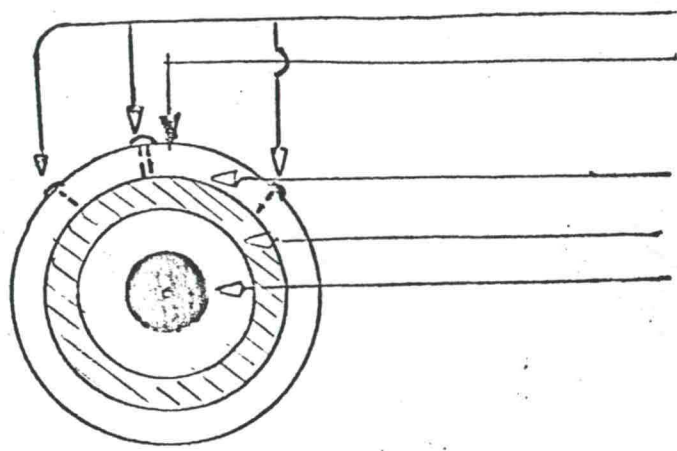
BRAZED JOINTS
NI SPHERE

UF_6 CHAMBER
LIF CONT.
SAMPLE

FE - NI ALLOY

.01" Cu
EACH INCH

LAMINATES 2"@ .01"

DUCTILE NI

SPHERICAL ELECTROFORMED
ISOSTATATIC PRESS
(NOT TO SCALE)

W.A.H. 10/17/75

DRAWING NO. 1