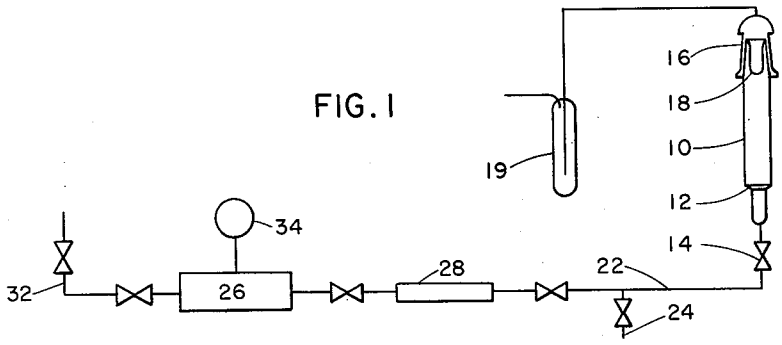
Jan. 15, 1963 W. ARBITER 3,073,698

DISPERSION HARDENING OF URANIUM METAL

Filed May 29, 1961

FIG. 1



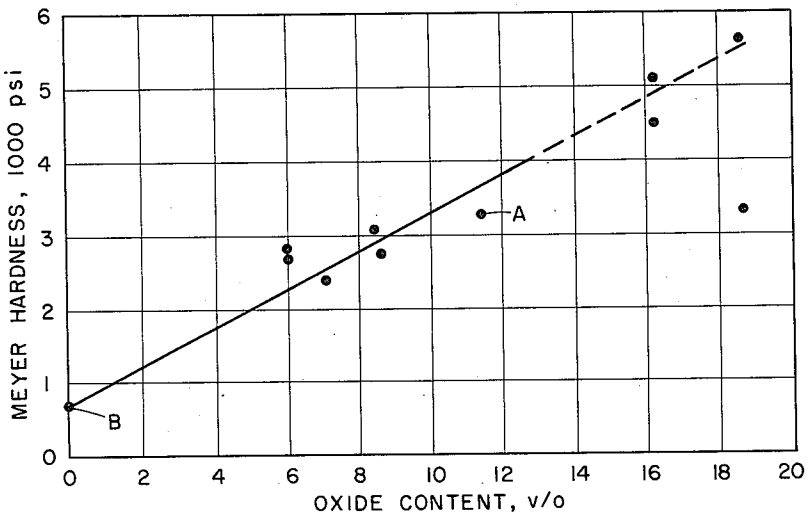


FIG. 2

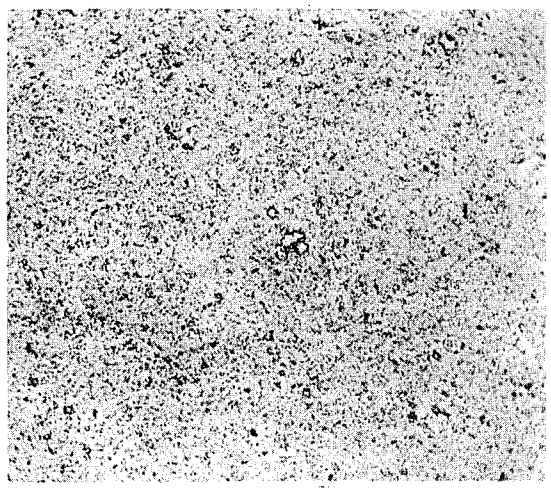


FIG. 3

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DISPERSION HARDENING OF URANIUM METAL

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The present invention relates to a method for hardening uranium metal and more particularly to a method of hardening uranium metal by forming therein a fine and uniform dispersion of uranium dioxide.

Metallic uranium is a desirable nuclear fuel material but the use of this material is restricted to relatively low temperatures and burn-ups due to certain inherent metallurgical limitations. For example, uranium exists in three separate phases, designated alpha, beta and gamma, depending on the particular range of temperature applied. The low-temperature, alpha phase uranium is somewhat malleable and has been described as "semiplastic" due to its low elasticity. Uranium in this phase is dimensionally unstable and so is not completely suitable for reactor use in this state. The medium-temperature, beta phase uranium is brittle, while the high-temperature, gamma phase is plastic and somewhat more suitable for reactor use than the other phases, especially the low temperature alpha phase.

As an example of the problems presented when pure uranium is used as a reactor fuel, under normal reactor opearting conditions both alpha and beta phases can exist simultaneously in the metal. With fuel core temperatures in the beta temperature range and the fuel skin in the alpha temperature range, distortion and ultimate failure of the fuel can result. This is because of the increase in volume on transforming to beta in the core which puts the skin under severe tensile stresses. Furthermore, fission gas formation at high temperatures causes considerable pressure exceeding the creep strength of the metal.

It has been found possible to minimize the low temperature thermal and radiation induced dimensional instabilities in unalloyed uranium by providing fine, randomly oriented grains in the metal. This is done either by beta heat treatment of cold worked uranium metal followed by quenching, or by the use of powder metallurgical techniques in the fabrication of the uranium. These measures, however, are only slightly helpful. Another approach is to make alloying additions to the uranium to stabilize the isotropic gamma phase, thereby avoiding the low temperature instability. However, since considerable quantities of molybdenum or niobium are required for stabilization of the gamma phase, these additions generally have an undesirable effect upon neutron economy. Therefore, a uranium-rich metallic fuel material having good elevated temperature strength properties and capable of high burn-up is still not available.

It has been suggested that the mechanism of dispersion hardening be utilized to solve this problem. By this technique, a large number of fine particles of a refractory material are uniformly distributed throughout the matrix of the parent metal. In order to be effective, however, the spacing between the particles of the dispersed phase must be small, about one micron or less. In addition, the dispersion must be stable, that is, not grow or agglomerate at the temperature of use. This requirement eliminates most precipitation-hardened alloys from consideration for high temperature applications, since in these alloys the precipitated phase is soluble in the matrix from which it was originally derived.

The best known dispersion-hardened product known is SAP, an aluminum base material made by means of powder metallurgy from surface oxidized fine aluminum. Attempts to apply this type of dispersion hardening to uranium metals have not proved successful, because no technique or method has been devised for successfully and accurately obtaining the proper degree of dispersion along with proper particle size as well as the desirable spacing of the dispersoid.

In the present invention, it is possible to apply the metal-metal oxide dispersion technique to uranium metal. The inventive method permits the exercising of close, complete and accurate control over the proper degree of dispersion, particle size, and spacing of the dispersoid. The dispersoid, which is UO_2 in the preferred embodiment of this invention, instead of being inserted as a separate ingredient into the uranium particles, is formed chemically in the pure metal as a surface film on very pure, finely divided uranium powder prior to the consolidation of the powder by powder metallurgical techniques. In order to obtain the uranium at a very finely divided pure and active state, the uranium is initially, in accordance with this invention, hydrided to form uranium hydride which results in a large volume increase causing the uranium hydride to powder as it forms on the surface of the uranium. The particle size may be made smaller by decomposing the hydride and repeating the hydriding step. The hydride powder thus formed is very active due to its fine particle size and large surface area. As a result, it is seen that the uranium metal powder which is later formed from the hydride in accordance with this process is likewise extremely active because of its highly divided state and large surface area, a fact which results in its sintering at temperatures as low as 600° F. when the hydride is decomposed. This sintering or agglomeration of the decomposed hydride means that a comminution step is required to bring the material back to a fine particle size. It is difficult, if not impossible, to perform such comminution and regain the fine particle size originally present in the hydride without contamination. However, to prevent such sintering from occurring, the hydride is exposed to a very dilute mixture of oxygen in an inert atmosphere to form initially on the fine uranium hydride particles a thin oxide film. The oxide skin thus formed prevents sintering or agglomeration of the uranium powder as it is formed during the decomposition of the hydride which is continued until completion. It is the presence of the thin oxide skin on each uranium particle which permits the retention of the fine particle size during the subsequent process steps and obtains many of the benefits of this invention as will be later described in more detail.

It is, therefore, a first object of this invention to provide a method for dispersion hardening uranium metal.

Another object of this invention is to provide a method for preparing a dispersion hardened uranium metal based on a metal-metal oxide system.

Still another object of this invention is the provision of a method of preparing uranium metal powder for use in reactor applications.

Another object is the provision of a method for dispersing UO_2 in a uranium matrix.

Still another object is to provide a method for controlling the degree of dispersion, particle size, and spacing of a UO_2 dispersoid in a uranium dispersion medium.

Another object of this invention is to provide a method for preparing a finely divided pure uranium powder having a controllable amount of uranium oxide on the surface in the form of a thin film.

Other objects and advantages of this invention will hereinafter become more evident from the following description of a preferred embodiment of this invention with reference made to the accompanying drawing in which:

FIG. 1 is a schematic diagram of apparatus suitable for carrying out the preferred method of this invention;

FIG. 2 shows a chart of the Meyer hardness of uranium plotted as a function of oxide content; and

FIG. 3 is a photomicrograph of a sample of dispersion hardened uranium prepared in accordance with this invention.

In a preferred form of this method, uranium is first hydrided to form uranium hydride (UH_3). This may be accomplished by loading uranium shot or lumps into a stainless steel container and then passing dry hydrogen into the container. Simultaneously, heat is applied to the container to carry out the desired reaction at 400 to 690° F. Hydriding of the uranium causes the final product to expand and powder with particles in the range of about 0.5 to 20 micron size. Repetition of the hydriding step after first decomposing the UH_3 particles under heat brings the average particle size into the lower part of this range with somewhat greater uniformity in the final product.

The next step of the process is carried out in the apparatus illustrated in FIG. 1, where is shown a heat resistant glass column **10** provided at the bottom with a fritted glass filter **12** and below this a vacuum stopcock **14**. At the top of column **10** is a ground glass joint **16** which permits column **10** to be sealed vacuum tight and in which a filter **18** is disposed. Column **10** exhausts through a bubble trap **19** as is understood in the art. The uranium hydride powder to be oxidized in accordance with this invention (as is to be more particularly described below) is placed in column **10** to rest on glass filter **12**, the operations being carried out in an inert atmosphere dry box. The tubulation **22** below vacuum stopcock **14** is connected to an inert gas manifold **24** which leads through the dry box wall (not shown). High purity tank argon is permitted to flow through column **10** from manifold **24**. After the proper argon flow conditions are established, as set forth below, oxygen is admitted into the argon stream from a calibrated volume **26** through a calibrated leak **28**. The oxygen supply is passed through a valve controlled manifold **32**, while calibrated volume **26** is provided with a pressure gauge **34**.

In utilizing the apparatus of FIG. 1 to carry out the next step of the method of this invention, column **10** is charged with the uranium hydride powder (prepared as previously described) after the powder weight is first determined. With column **10** charged with the uranium hydride, the quantity of oxygen required to yield the desired oxide content is calculated and the calibrated volume **26** is filled with the required amount of oxygen at some desired pressure, i.e., 20 p.s.i.g. Then from manifold **24**, argon is admitted under suitable pressure into the reaction column **10** and the flow rate is established to provide agitation of the powder bed therewithin.

When the agitation is established, oxygen is permitted to bleed into the argon stream through calibrated leak **28** at a very low rate of flow to prevent burning. A thermocouple (not shown) attached to the outside surface of column **10** adjacent to the powder bed may be used to record the temperature of the column. When the temperature of column **10** reaches a peak and begins to fall off, the oxidation is interrupted by cutting off the supply of oxygen. If the total column weight of the powder is obtained again, the difference, of course, between the two weights represents the oxygen pickup. This initial oxidation step, which is more or less self regulating, may be referred to as the preoxidation step of this process, and results in thin stoichiometric or non-stoichiometric uranium oxide coatings on the UH_3 particles in the powder. When the temperature peak mentioned above is reached the surface oxidation is completed and the reaction does not continue. This pre-oxidation step results in the preservation of the fine particle size of the uranium powder during the remainder of process because the thin UO_2 coatings prevent sintering of the uranium metal which normally occurs at temperatures as low as 600° F. in this finely divided and active state. The preoxidation step may be carried out at ambient temperatures and up to as high at 250° F. if desired.

In order to convert the UH_3 particles contained within the UO_2 into pure uranium, the pre-oxidized uranium hydride powder is heated in vacuum to 600°–700° F. During this treatment, the bulk of the hydrogen is removed but because of the high density oxide skin, the rate of the removal is slow. The elimination of the hydrogen from the lattice permits additional oxygen to be adsorbed during subsequent oxidation operations.

After the hydrogen is removed, the procedure outlined in the preoxidation step is repeated until all the premeasured amounts of oxygen are absorbed. With the hydrogen removed, the oxygen penetrates the UO_2 layers to oxidize the uranium directly underneath. It has been found that the final oxide content of the material can be controlled to within 1–2 volume percent, while the final UO_2 content may be varied by this process from 1 to 30 volume percent. With the pre-oxidation step of the hydride being self-controlled, it is actually the subsequent, final oxidation step after the decomposition of the preoxidized hydride particles which permits the proper amount of oxygen to be added to obtain the final desired relationship between oxide and pure uranium.

After the UO_2—U powder is produced in accordance with this invention, the final dispersion hardened product is prepared by hot or cold pressing in accordance with known technques.

EXAMPLES

A large number of runs were made carrying out the process described above and they may be illustrated by the following examples.

Uranium shot was hydrided as described with reaction temperatures in the range of 400° to 690° F., producing UH_3 particles of 0.5 to 20μ size, as already indicated. A typical example is one batch which was hydrided at a beginning temperature of 560° F., and final particle size of 4.5μ. Another example with a rehydriding step added produced a final product size of 1.9μ. It should also be pointed out that uranium in any form initially, such as 3" bars of uranium cylindrical stock, will produce the same effect as far as the UH_3 powder is concerned and may be used.

Table I lists data of several runs of uranium hydride prepared in column **10** (FIG. 1) in which the calibrated volume was filled with oxygen to 20 p.s.i.g. and the oxygen was permitted to bleed into the argon stream through the calibrated leak at from 10 to 12 cm.^{3} of oxygen per minute depending on the pressure. It will be seen that the total volume percent of UO_2 (v/o of UO_2) calculated and as desired are reasonably close. While the oxidation steps shown in the table below were carried out at ambient temperatures, other tests indicate that these steps could, if desired, be carried out at elevated temperatures at least up to 250° F.

Table I

Preoxidation		Final Oxidation		Total v/o UO_2	
Δw.	calculated	Δw.	calculated		
g. O/g. U	v/o UO_2	g. O/g. U	v/o UO_2	Desired	Actual
0.00152	2.15	0.00412	7.50	10	9.65
0.00124	1.80	0.00301	6.05	7.5	7.85
0.00148	2.10	0.01215	16.50	17.5	18.60
0.00141	2.00	0.00352	5.00	7.5	7.00
0.00164	2.35	0.00640	9.00	12.5	11.35
0.00131	1.90	0.01024	14.00	17.5	15.90
0.00374	5.20	0.00783	11.20	17.5	16.40
0.00440	6.20	0.00806	11.30	17.5	17.50
0.00272	3.80	0.00938	13.00	17.5	16.80

TESTS

A series of tests on the dispersion hardened uranium metal prepared from powders made in accordance with

the method described above were performed to determine how the physical characteristics of pure uranium compared with the characteristics of the dispersion hardened materials. The UO_2—U dispersions described were prepared for these tests by hot pressing and extruding the powdered product.

For example, high temperature, or gamma phase, extrusions were prepared, and these were subject to analysis and testing. FIG. 2 is a graph showing the relationship between hardness of the final product after extrusion as a function of oxide content. Point A represents a sample which was selected for metallographic examination. In FIG. 3 is shown a photomicrograph of this specimen having 11.4 v/o UO_2, as polished, at 500×. This specimen shows a close approach to an ideal dispersion-hardened microstructure, although there are some areas relatively devoid of the oxide phase. Point B in FIG. 2 represents the hardness of unalloyed uranium without any oxide content for comparison with the samples with oxide content prepared in accordance with this invention.

Other tests on these samples were run, including alpha-beta thermal cycling and transverse creep measurements under load. These may be briefly summarized in Table II in which a sample with 16.5 v/o of UO_2 prepared in accordance with this invention is compared to an unalloyed pure uranium control:

Table II

	Unalloyed U	16.5 v/o UO_2
Meyer hardness, p.s.i.[1]	715	5,130.
Transverse creep, rate, in./hr	[2] 1.5	[3] 0.028.
Alpha-beta cycles to failure	30–50	No failure after 105.

[1] 3.5 lb. load at 1500° F. applied for 15 minutes in vacuum.
[2] Max. fibre stress 1330 p.s.i. at 1700° F. for 5 minutes.
[3] Max. fibre stress 4040 p.s.i. at 1740° F. for 30 minutes.

Summarizing the results of the samples and tests, the extent of the oxidation can be controlled to yield a product containing from 1 to 30% volume of UO_2, and the material thus formed is ideally suited for hot pressing and extrusion. This extrusion may be accomplished for example with a reduction ratio of ten to one at a temperature of 1500° to 1700° F. with pressures at 10,000 to 22,000 p.s.i. This achieves a dense dispersion hardened uranium having good hot strength, hardness and good thermal cycling and irradiation behavior.

It is thus seen that there has been provided a method for successfully producing a U—UO_2 dispersion in which the oxide content is controlled to a high degree. Further, the process retains fine particle size which is important for obtaining a matrix having good mechanical and nuclear properties. Further, it has been demonstrated in accordance with this invention that, after being hot pressed and extruded, under certain conditions, dense dispersion hardened compositions can be made containing up to 30% volume of oxide.

In effect, this invention permits the controlled oxidation of finely divided uranium particles accomplished in a uniform manner to an extent not heretofore found possible. This permits the use of unalloyed uranium as a metallic nuclear fission fuel material having good elevated temperature strength properties capable of high burn-up. It also provides for the first time a way of

applying the well-known dispersion hardening approach along with its advantages to the treatment of uranium. Also, the method permits to a certain extent the selection or the final physical characteristics because it permits the amount and thickness of the coatings of the UO_2 to be preselected in advance with the advantages already noted.

While only a preferred embodiment of this invention has been described, it is understood, of course, that the invention may be practiced in accordance with the scope of the appended claims.

What is claimed is:

1. The method of dispersing UO_2 in a uranium matrix comprising the steps of preparing a bed of fine particles of UH_3, passing small amounts of oxygen mixed with an inert gas through said bed until all of said particles are coated with thin layers of UO_2 as a result of a chemical exchange, and heating said bed to decompose said UH_3 particles causing the escaping hydrogen to pass out through said thin layers of UO_2, leaving a bed of unsintered fine uranium particles coated with UO_2.

2. The method of claim 1 in which the oxygen is added in minute amounts at a temperature ranging from ambient up to 250° F.

3. The method of claim 1 in which the bed of coated UH_3 particles is heated in a vacuum at 600°–700° F. to remove the hydrogen.

4. The method of claim 1 in which additional oxygen is added to said bed after decomposition of said UH_3 particles to further oxidize the coated uranium particles and thereby thicken the UO_2 coatings on said particles.

5. The method of claim 1 in which the sizes of the UH_3 particles range from 0.5 to 20μ.

6. The method of preparing a dispersion of UO_2 in a uranium matrix comprising the steps of preparing an agitated bed of fine UH_3 particles by flowing an inert gas therethrough, preoxidizing said particles by adding small amounts of oxygen to said inert gas until said UH_3 particles are coated with UO_2 as a result of a surface chemical exchange, heating said coated UH_3 particles at a temperature sufficient to decompose said UH_3 until substantially all of the hydrogen has been freed thereby leaving a bed of unsintered uranium particles coated with UO_2, and further oxidizing said uranium particles by agitating and flowing further oxygen mixed with said inert gas through said bed until the desired content of UO_2 is reached.

7. The method of claim 6 in which the preoxidation of said particles is terminated when the temperature of said bed reaches a peak value and begins to decline.

8. The method of claim 6 in which the bed of UH_3 particles is prepared from uranium which has been hydried to form UH_3 which powders during its formation into a very fine particle size.

9. The method of claim 8 in which the UH_3 is decomposed under heat and the hydriding step is repeated.

10. The method of dispersion hardening uranium metal comprising the steps of adding oxygen to a matrix of uranium hydride particles being 0.5 to 20μ in size sufficient to form a uniform dispersion of UO_2 in the range of 1 to 30% by volume throughout said matrix and work hardening said dispersion by extruding the latter.

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