Feb. 18, 1969 A. ACCARY ETAL 3,428,717
Filed July 9, 1965

METHOD OF EXTRUDING METALLIC CARBIDES AND IN PARTICULAR URANIUM MONOCARBIDE

Fig.1.

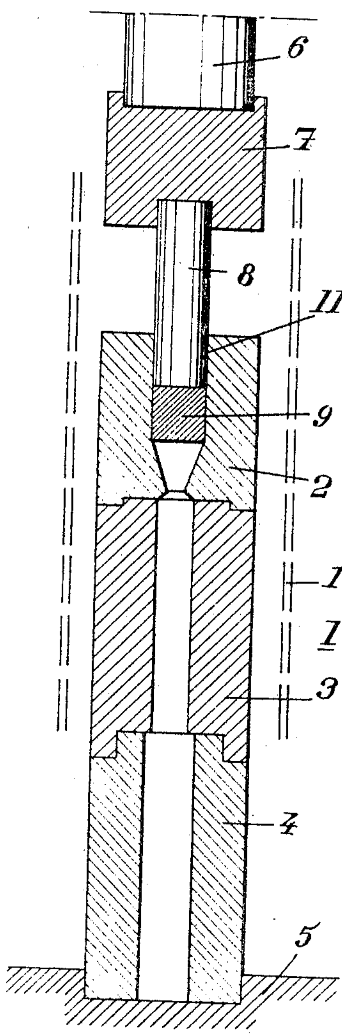

Fig.2.

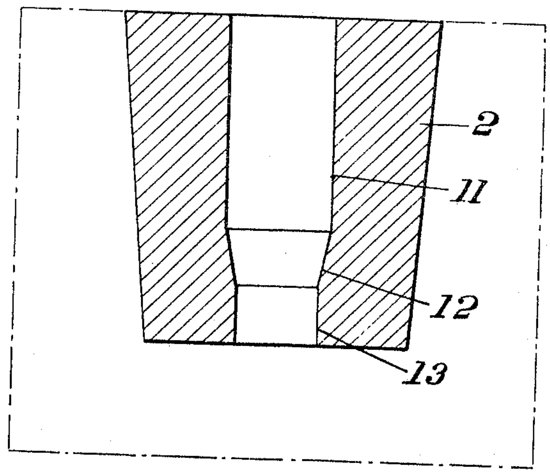

Fig.3.

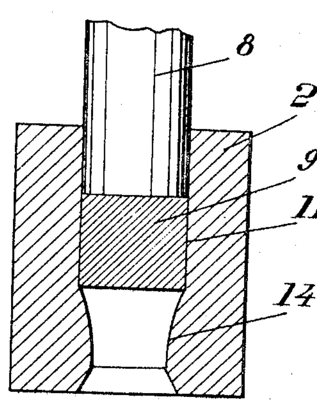

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Fig. 5.

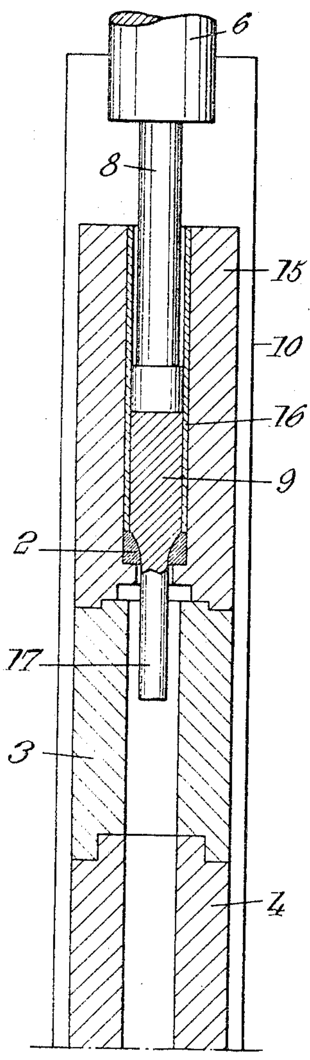
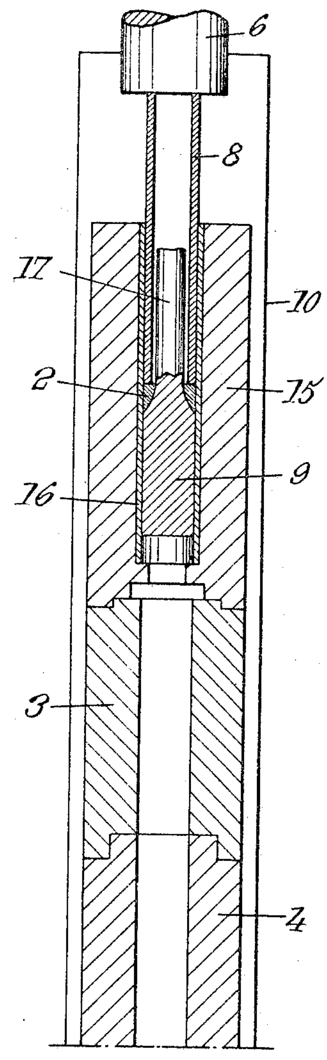


Fig. 4.



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METHOD OF EXTRUDING METALLIC CARBIDES AND IN PARTICULAR URANIUM MONOCARBIDE

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Int. Cl. B29f 3/04

ABSTRACT OF THE DISCLOSURE

The method of extrusion of a metal carbide piece comprises extruding this piece in the hot state through a graphite die of high mechanical resistance.

The present invention relates to methods of shaping by extrusion, metallic carbides and in particular uranium monocarbide. The invention is also concerned with apparatus for carrying out these methods.

The chief object of the present invention is to obviate the difficulties of such a shaping and to permit of obtaining products of better quality than those obtained up to the present time.

The essential feature of the present invention consists, in order to ensure the extrusion in the hot state of the above mentioned products, in making use of graphite dies.

Another feature of the present invention consists in using with the above mentioned graphite dies, a rate of extrusion at least equal to two, preferably ranging from 2.8 to 10, the temperature being itself higher than 1600° C., preferably ranging from 2200 to 2400° C. and advantageously from 2250 to 2350° C. and the pressures ranging from 200 to 800 kgs./cm.^{2}, and in particular being substantially of 350 kgs./cm.^{2}.

Still another feature of the present invention consists in performing the extrusion from uranium or other carbides obtained by carbothermy, that is to say by reaction in a vacuum, at high temperature, of a preliminarily compressed mixture of a powder of oxide of uranium or another metal and of graphite.

Preferred embodiments of the present invention, will be hereinafter described with reference to the appended drawings, given merely by way of example, and in which:

FIG. 1 is a diagrammatic sectional view of an extrusion press for carrying out the method according to the present invention;

FIGS. 2 and 3 are sectional views illustrating modifications;

FIGS. 4 and 5 are sectional views of two other modifications.

It will be supposed in the following description that the object of the invention is to shape an uranium carbide piece by extrusion in the hot state, from either a preliminarily molten product or from a low density carbide prepared by carbothermy in the solid state.

It has been noted that uranium carbide has an important capacity of deformation when treated at temperatures above 1600° C. and in particular above 2200° C., so that it seems advisable to shape this carbide by extrusion in the hot state in a die where it is subjected to a high pressure.

As a rule, it seems necessary to provide pressures of the order of 250 kgs./cm.^{2} and even more (up to 1000 kgs./cm.^{2} for instance) so that the dies must be chosen so as to be capable of resisting this particular temperature and pressure conditions.

It has been found, as a result of experiments, that graphite is particularly suitable for making these dies.

Graphite has a high mechanical resistance (compression breaking load averaging 3000 kgs./cm.^{2} at 2500° C. and traction breaking load averaging 1500 kgs./cm.^{2} at the same temperature), which enables it to resist extrusion efforts.

As shown by FIG. 1, for the extrusion of uranium carbide fed from a furnace **1** where a vacuum is provided, use is made of a graphite die **2**, mounted on supports **3** and **4**, advantageously of graphite and bearing upon the hearth of the furnace. The pressure is exerted by means of jack piston **6**, which controls, through an intermediate block **7** of graphite, a ram **8** itself, of graphite, a billet to be extruded being shown at **9**. The whole is surrounded by a heating element **10**.

Concerning die **2**, it is made for instance of high mechanical resistance graphite and its active surfaces are given a suitable shape.

According to the embodiment of FIG. 2, the die comprises, after a cylindrical portion **11**, a core **12** followed by a cylindrical duct **13**.

According to the embodiment of FIG. 3, which gives the best results, there is a convergent part **14** having substantially the shape of a hyperboloid of revolution, as shown.

Examination, and in particular macroscopic examination has shown that, by making use in particular of a die of the type of FIG. 3, good results were obtained with temperatures ranging from 2200 to 2400° C., and especially from 2250 to 2350° C., and pressures ranging from 220 to 800 kgs./cm.^{2}, possibly of 1000 kgs./cm.^{2}.

Uranium monocarbide will be preferably chosen either of a composition close to the stoichiometric composition (the UC product corresponding to 4.8% by weight of carbon) or of hyperstoichiometric composition (the proportion of carbon being higher than 4.8% and being possibly equal to 6% and even more). It would also be possible to apply the method according to the invention to the extrusion of uranium dicarbide UC_2 (the proportion of carbon being 9.16%).

Rough pieces of monocarbide of sub-stoichiometric composition, therefore containing free uranium, give generally rise to a speed of extrusion lower than that obtained with pieces of over-stoichiometric composition, in particular due to the tendency, for said first mentioned pieces, to the formation, by reaction with the graphite of the die, of a superficial layer of uranium dicarbide UC_2, which causes a seizing tending to slow down the extrusion. As it will be hereinafter indicated, it is possible to remedy this difficulty by a preliminarily lining of dicarbide.

The speed of extrusion, which is for instance, in a press such as above described, of the order of 2 mm. per minute for an alloy containing 4% of carbon, passes to 3 mm. per minute for alloys containing from 4.7 to 4.9 of carbon. It may be as high as 20 mm. per minute for alloys containing 9% of carbon (UC_2).

However it should be noted that another parameter is to be considered, to wit the ratio of extrusion (ratio of the cross sections before and after extrusion, respectively).

It seems that the minimum ratio should be of the order of magnitude of 2, in particular from 2.8 to 3, this ratio being possibly as high as 10. For instance, excellent bars, of a diameter ranging from 6 to 10 mm. and even more, have been obtained by extrusion, by means of the die of FIG. 3, and with a ratio of extrusion equal to 10.

The compacity is the better as the extrusion rate is higher.

It is of great interest to make microscopic studies to determine whether contact with graphite did not lead to a noxious superficial pollution.

Such studies have shown that extrusion in a graphite press permits of obtaining excellent products, with a preferred crystallographic direction parallel to the axis of extrusion.

It is true that in the case of alloys containing free uranium (sub-stoichiometric alloys) a dicarbide superficial layer appears, with a tendency to cracking, but it is possible to obviate this disadvantage by means of a dicarbide lining as it will be hereinafter described.

According to a particularly advantageous embodiment of the invention, extrusion is performed on uranium carbide produced by the reaction in a vacuum of uranium oxide UO_2 and of graphite, this reaction taking place at temperatures averaging 1800° C. and in substantially stoichiometric proportions.

For instance, uranium oxide and graphite in the powder state are first mixed together when cool and compressed under loads averaging 3–4 tons per cm.^{2}, which permits of obtaining, for instance, small compact cylinders, or pellets.

Said cylinders are then heated to 1800° C. for some hours so that the reaction of formation of the carbide is as complete as possible. Their density is then about 50% of the theoretical density.

These cylinders are used for feeding a die of the above mentioned type, the results that are obtained being of the same order as those already indicated, as it was found for instance by treating, in the press, pellets under a load generally higher than 250 kgs./cm.^{2}, in particular of 350 kgs./cm^2.

The grain that is obtained is substantially finer than in the case of products that have been preliminarily molten.

The extrusion of such pieces, that is to say of porous pellets of a density equal to about 50% of the theoretical density, takes place in two successive steps:

A compression at decreasing speed, which is in fact a compacting of the initial product without true extrusion taking place, and

Final extrusion at a higher output rate.

Other features permitting to carry out the invention in particularly advantageous conditions will now be described.

According to one of these features the press is made in several portions so as to avoid the necessity of replacing the whole of it after deterioration of its active surfaces.

For instance such a press includes, as shown by FIG. 4;

(a) A hooping tube **15**, made of graphite of high mechanical resistance;

(b) A ram **8**, also of graphite of high mechanical resistance, subjected to the action of a jack piston **6**;

(c) A jacket **16**, also of graphite, but of a quality which may be lower since this jacket is intended to be replaced whenever necessary, and

(d) A die **2** which is also made of high resistance graphite.

In such a system, the hooping tube **15** is intended to support most of the mechanical effort of extrusion, whereas jacket **16**, relatively thin, for instance 2 mm. thick, does not participate or participates little, in the resistance of the whole. This is why it must be made of graphite of ordinary quality.

The function of this jacket is to be able to comply with the working conditions, generally characterized, chiefly in the case of sub-stoichiometric alloys, by a tendency to the formation of UC_2 and to seizing.

Besides it may happen that this jacket gets broken during extrusion along one or several generatrices. It should be noted that, in this case, this breaking facilitates the mounting of this jacket, which is effected merely by exerting a relatively small force, upon the end of the press. It becomes possible, in this condition, to reutilize the hooping tube and the ram, which are the most expansive pieces of the whole.

FIG. 4 shows, with the same reference numerals as FIG. 1, a heating capacity **10** and intermediate supports **3** and **4**, advantageously made of graphite. The rough piece is shown at **9** and the bar obtained after extrusion at **17**.

According to another feature of the invention the method is carried out in such manner that the extrusion work can be effected from the beginning upon a layer of uranium dicarbide.

It has been stated above that extrusion gives rise, in particular for alloys where the percentage of carbon is lower than 4.8%, therefore with free uranium, to the formation of UC_2. The extruded products comprise in this case a superficial layer consisting mostly of dicarbide and separated from the heart of bar **17** by a zone of cracks. The formation of these cracks is due to the differences between the expansion coefficients of the dicarbide and of the monocarbide respectively.

This layer is perhaps not dangerous because it can be easily removed when proceeding to a surface machining but such a layer contributes in producing in the press, when it is formed, a seizing which reduces the speed of extrusion.

By preliminarily interposing a layer of dicarbide, it is possible to remedy this phenomenon, which eliminates the above mentioned drawback and further permits of using sub-stoichiometric alloys, possibly even at lower extrusion temperatures, for instance averaging 2000° C., by taking advantage of the greater deformability of this substoichiometric alloys.

Concerning said preformed layer it may be provided either on the surfaces of the press or on the piece **9** to be treated.

In this last case, a layer of UC_2 is deposited upon the rough pieces, the thickness of this layer depending upon the ratio of extrusion being for instance of 1 mm. on the radius for a ratio of extrusion of 8 and a rough piece of a diameter ranging from 20 to 40 mm. by covering them with a suspension of UC_2 in collodion or another organic liquid, or in any other way. It is thus possible to treat, in particular, rough UC pieces obtained by carbothermy, that is to say by heating and sintering of UO_2 and carbon pellets.

It should be noted, as a supplementary advantage of this dicarbide layer, that it constitutes on the surface of the extruded products a kind of plating which has for its consequence to limit the gradient of concentration in carbon, from the outside toward the inside of the product, due to which the cracks are produced.

The invention further comprises another feature which will now be examined and which also opposes another case of formation of cracks when the product is cooled down upon leaving the press.

When using a press of the kind of that of FIGS. 1 and 4, it is found, by macrographic examination, that some cracking takes place superficially, chiefly when, as it is most frequent, there is formed an external layer of uranium dicarbide. Such cracks are partly due to the fact that the bar is often subjected, when leaving the die, to a cooling which is too quick.

As a matter of fact, if the external layer of the bar is subjected to a cooling taking place more quickly than for the internal zone, these two zones expand differently so that stresses are produced which may result in breaks of the external layer. These phenomenons are more intensive in the case of a dicarbide external layer because the coefficient of expansion of dicarbide is different from that of monocarbide.

According to the present invention the thermal gradients are reduced by using an inverted extrusion method, by means for instance of a press of the kind of that of FIG. 5.

In such a press, ram **8** is hollow and drives die **2** ahead thereof so that the bar is caused to issue through the inside of said ram **8**.

The extruded product is thus wholly surrounded by the die and the ram, which constitute a natural heat insulation. Furthermore, in this case, the extruded product is at the same temperature over its whole length, this temperature being that produced by the heating means **10**.

It should be well understood that the invention may apply to the treatment of all dicarbides, such as thorium, plutonium, tungsten, mixed thorium and uranium carbides.

It is also possible to extrude uranium dicarbide UC_2 (9% of carbon) which gives rise to no cracking since there is no reaction with the graphite of the press.

The method according to the present invention has the following advantages:

Possibility of obtaining excellent products,

Possibility of providing apparatus having a great time of utilization, especially when there are made as shown by FIGS. 4 and 5,

Possibility of treating in good conditions given alloys having a low percentage of carbon, when a graphite layer of dicarbide is used,

Possibility of reducing the causes of superficial cracking.

In a general manner, while the above description discloses what are deemed to be practical and efficient embodiments of the present invention, said invention is not limited thereto as there might be changes made in the arrangement, disposition and form of the parts without departing from the principle of the invention as comprehended within the scope of the appended claims.

What we claim is:

1. A method of extruding a piece of a metal carbide which comprises performing extrusion of said metal carbide piece in the hot state through a die of high mechanical resistance graphite.

2. A method of extruding a blank of uranium monocarbide which comprises performing extrusion of said uranium monocarbide blank in the hot state through a die of high mechanical resistance graphite.

3. A method according to claim **1** wherein the temperature at which extrusion is performed is higher than 1600° C., the extrusion operation being performed in a vacuum.

4. A method according to claim **1** wherein the temperature at which extrusion is performed ranges from 2200 to 2400° C., the extrusion operation being performed in a vacuum.

5. A method according to claim **1** wherein the temperature at which extrusion is performed ranges from

2250 to 2350° C., the extrusion operation being performed in a vacuum.

6. A method according to claim 2 wherein the pressure under which extrusion is performed ranges from 200 to 800 kgs. per sq. cm.

7. A method according to claim **1** wherein the pressure under which extrusion is performed is 350 kgs. per. sq. cm.

8. A method according to claim **1** wherein the ratio of the cross sections of the piece respectively before and after extrusion, is at least equal to 2.

9. A method according to claim **1** wherein the ratio of the cross sections of the piece respectively before and after extrusion, ranges from 2 to 10.

10. A method according to claim **1** wherein the monocarbide that is treated is close to the stoichiometric proportions of carbon and uranium.

11. A method according to claim **1** wherein the monocarbide that is treated is sub-stoichiometric, containing from 4 to 4.8% of carbon.

12. A method according to claim **1** wherein the monocarbide that is used is hyperstoichiometric.

13. A method of extruding a piece of uranium dicarbide which comprises performing extrusion in the hot state of a blank through a die of high mechanical resistance graphite.

14. A method which comprises forming a layer of uranium dicarbide on an uranium carbide blank and extruding the blank thus prepared and in the hot state through a die of high mechanical resistance graphite.

15. A method according to claim **14** wherein said layer is formed by coating said blank with a suspension of uranium dicarbide in collodion.

16. A method of extruding a piece of a metal carbide which comprises performing extrusion of said metal carbide die in the hot state through a die of high mechanical resistance carbon the active surface of which is in the form of a hyperboloid of revolution.

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