METHOD OF MAKING CARBIDE-COATED GRAPHITE DIES AND COATED ARTICLE


Filed Apr. 20, 1961, Ser. No. 104,466

Claims priority, application Great Britain, Aug. 23, 1956, 25,822/66
5 Claims. (Cl. 117—5.1)

This invention relates to improvements in dies and is particularly concerned with improvements in graphite dies for use in high temperature hot pressing processes which are performed at temperatures above 1000° C., e.g., up to about 2300° C., and in a method of producing same.

This application is a continuation-in-part of copending application Ser. No. 579,987, filed Aug. 31, 1961, "Method of Making Carbide Coated Graphite Dies and Coated Article," filed August 21, 1957, now abandoned.

Dies for use in high temperature hot pressing processes which are performed at temperatures above 1000° C. are commonly made of graphite in view of the resistance of this material to the high temperatures and pressures involved. In some cases, however, the material to be hot pressed may be one which either reacts with or is mutually soluble in the material of the die at the pressing temperature and in these cases there is a tendency for the hot pressed body to stick to the die. Where such sticking occurs the least harmful result is that a new die has to be used for each pressing operation thereby adding considerably to the cost. It is quite possible, however, that sticking may cause the die to break before the pressing operation is completed, or it may result in the pressed body breaking during cooling as a result of the differential contraction of the die and the body.

It is an object of the present invention to provide an improved die for use in high temperature hot pressing processes which shall not be subject to the disadvantages referred to.

According to one feature of the present invention the surface or surfaces of the wall or walls defining the cavity in a graphite die for use in a high temperature hot pressing process is or are coated with a film of a carbide of one of the transition elements in Groups IV, V and VI of the Periodic System.

The carbide is preferably titanium carbide.

According to another feature of the present invention, a method of manufacturing a graphite die for use in a high temperature hot pressing process comprises the step of coating the surface or surfaces of the wall or walls defining the die cavity with a film of a carbide of one of the transition elements in Groups IV, V and VI of the Periodic System.

The carbide is preferably titanium carbide and it may be applied to the surface or surfaces in the form of a suspension of titanium carbide in butyl titanate paint medium and subsequently fired on to said surface or surfaces. Alternatively the film of titanium carbide may be produced by heating the die, which is of graphite, and pasting a mixture of vaporized titanium and hydrogen over the surface or surfaces to form the film of titanium carbide thereon. Preferably the film of titanium carbide is fired on to the surface or surfaces e.g., by heating the die to a temperature of the order of 2000° C. in an atmosphere of hydrogen.

In another embodiment of the invention, the carbide coating is applied to the graphite die surface in a moistened condition either by contacting the die cavity or bare surface or surfaces with an aqueous slurry of the carbide, or by sprinkling carbide dust onto the previously wetted die cavity surface. When the carbide is applied in a moistened condition the coating is fired in situ; that is, the coating is fired onto the die surface during the hot pressing operation. The powder or material to be hot pressed is loaded into the die after coating the die cavity surface as above described, and the loaded die is then placed into a hot pressing assembly. As the assembly is brought up to the hot pressing temperature, the moisture is removed from the carbide coating, and the coating is fired onto the die cavity surface.

The invention will now be described by way of example reference being made to the accompanying drawings in which:

FIGURE 1 illustrates diagrammatically one way of carrying the invention into effect,
FIGURE 2 is a view similar to FIGURE 1 illustrating a modification,
FIGURE 3 is a view similar to FIGURE 1 illustrating a further modification,
FIGURE 4 is a sectional view taken on the line IV—IV of FIGURE 5 of a cylindrical die according to the invention, and
FIGURE 5 is a section taken on the line V—V of FIGURE 4.

The surface or surfaces of the wall or walls defining the cavity of a graphite die may be coated with a film of a carbide of one of the transition elements in Groups IV, V and VI of the Periodic System by coating the surface or surfaces with a paint composed of the carbide of the transition element suspended in a suitable medium, the film so produced being allowed to dry and being fired on to the surface at an appropriate temperature in a protective atmosphere. Alternatively a film of the carbide of one of the transition elements in Groups IV or V may be produced by vaporizing or subliming, as the case may be, the tetrachloride of the transition element and passing it in admixture with hydrogen over the surface or surfaces of the die whilst the latter is heated to a temperature sufficient to cause the graphite of the die to react with the tetrachloride of the transition element to produce the carbide of the latter with the formation of hydrogen chloride due to the hydrogen present in the gaseous mixture, the carbide being deposited as a film of sublimed thickness on the surface or surfaces and desirably being subsequently fired thereon at an appropriate temperature in a protective atmosphere. A film of the carbide of a transition element in Group VI may be produced on the surface or surfaces of the wall or walls defining the die cavity by exposing the previously coated or bare surfaces to a gaseous mixture of hydrogen and the carbonyl of the transition element at a reduced pressure of from 0.1 to 10 mm. of mercury and heating the die to a temperature sufficient to cause the hydrogen to reduce the carbonyl to produce the carbide of the transition element which carbide is deposited as a film of substantially uniform thickness on the surface or surfaces. The carbide film is then subsequently fired on to the surface or surfaces at a temperature between 2000° C.—2100° C. in a protective atmosphere e.g., hydrogen. When the carbide coating is applied by contacting the die surface with an aqueous slurry of the carbide or by dusting onto a previously wetted die surface, the firing may alternatively be effected after the powder to be pressed is loaded into the die and during the high temperature hot pressing operation.

An example of the first of these methods is as follows: a paint composed of titanium carbide suspended in butyl titanate paint medium is prepared by ball-milling the titanium carbide in the butyl titanate for some hours, e.g., 8 hours. The surface or surfaces of the wall or walls defining the die cavity is or are then painted with the suspension and the film so produced is allowed to dry for one or
more hours. The film is then fired on to the surface or surfaces by heating the die to a temperature of the order of 2,000° C. or more in hydrogen. Butyl titanate is preferred as the paint medium because its ultimate decomposition product is titanium dioxide which is reduced to give titanium carbide during the high temperature firing operation.

The method of producing a film of the carbide of a transition element in Group IV or V using the tetrahedral transition element is based on the reaction $\text{MCl}_4 + \text{C} + \text{H}_2 = \text{MCl}_4 + 4\text{HCl}$ (where $\text{M}$ is the transition element) which can, under suitable conditions, produce a film of the carbide of the transition element on carbon. An example of coating the surface or surfaces of the walls or walls of a graphite die with titanium carbide by this method is as follows: Liquid titanium tetrachloride (FIGURE 1), contained in a suitable glass vessel 2, is heated to a temperature of 100° C. in a water bath 3 and hydrogen is passed through it at about 4 litres per minute from a source 4 of hydrogen under pressure by way of a tube 5 one end of which is immersed in the liquid titanium tetrachloride. A tap 6 is connected in the tube 5. The glass vessel 2 is closed by a glass plug 7 through which extends a tube 8 opening into the space above the liquid titanium tetrachloride in the vessel 2 and communicating with the interior of a cylindrical graphite die 9. A branch tube 10 connects the inside of the die 9 to the hydrogen source 4 and a tap 11 is connected in the tube 10. The hydrogen source 4 is connected to both the tubes 5 and 10 by a common tube 12 in which there is provided a further tap 13 whereby the hydrogen source may be isolated from the rest of the system. The die 9 is heated in any suitable manner, for example, by the electric heating coil 14 shown in FIGURE 1 which is connected by way of terminals 14 to a suitable source of supply.

The water-bath 3 vaporizes the titanium tetrachloride and, with the taps 6 and 13 open and the tap 11 closed, a mixture of vaporized titanium chloride and hydrogen flows into the cavity or interior of the die 9 so that the surface of the wall thereof is exposed to this mixture. The die 9 is heated by the coil 14 to a temperature of from 1500° C. to 1600° C., e.g., 1535° C. and the mixture of vaporized titanium chloride and hydrogen is caused to flow through the die 9 for a period of one to two hours, e.g., one hour. The end of the die 9 remote from the tube 8 is restricted by a plug and the gas issue from this end as a jet which is ignited. During the period referred to the carbon of the die reacts with the titanium tetrachloride to form a film of titanium carbide on the internal wall of the die 9 and at the end of this period the tap 6 is closed and the tap 11 is opened so that the supply of vaporized titanium tetrachloride is discontinued and hydrogen only passes to the interior of the die 9, the latter now being heated by the coil 14 to a temperature of about 2050° C. for a short period of the order of 15 minutes and then being allowed to cool, the hydrogen atmosphere being maintained during the cooling of the die. This high temperature heating improves the adherence of the titanium carbide to the die and removes any free titanium metal which might be present in the film by converting it to the carbide.

The procedure described above may be used to coat the interior of the die 9 with vanadium carbide by substituting vanadium tetrachloride for the titanium tetrachloride in the vessel 2.

Where the tetrachloride of the transition element is a solid which sublimes such as in the case of zirconium tetrachloride the procedure described above is modified as shown by FIGURE 2 by substituting a copper tube 15 for the vessel 2 and water bath 3. Like reference numbers are used to indicate like parts in FIGURES 1 and 2. The zirconium tetrachloride is disposed in the copper tube 15 and is heated by any suitable means such as, for example, a tubular wire wound resistance furnace indicated very diagrammatically by the heating coil 16, to a temperature of from 250° C. to 300° C., e.g., 270° C. and hydrogen gas is passed through the tube 15 for a period of one to two hours as before and the mixture of hydrogen and zirconium tetrachloride passed into the die 9, which latter is in this case maintained at a temperature of between 1700° C. and 1900° C. During this period the zirconium tetrachloride reacts with the carbon of the die to form zirconium carbide as a film on the interior of the die 9 and at the end of the period the tap 6 is closed and the tap 11 is opened so that hydrogen is supplied to the interior of the die 9 whilst the latter is now heated by the coil 14 to a temperature of at least 2100° C. for a short period of the order of 15 minutes after which it is allowed to cool whilst maintaining the atmosphere of hydrogen.

The method of producing a film of the carbide of a transition element in Group VI using the carbonyl of the transition element is as follows: The die 9 (FIG. 3) is disposed in a vacuum furnace 17 the interior of which is connected by a pipe 18 through a tap 19 to a vacuum pump 20. The interior of the furnace 17 is also connected by a pipe 21 through a tap 22 to a container 23 containing the carbonyl of the transition element, e.g., molybdenum carbonyl (Mo(CO)_6) which is solid at normal temperature and pressure. The interior of the container 23 is connected by a tap 25 to a source 26 of hydrogen under pressure. The die 9 is heated to a temperature of about 500° C. and the tap 19 is opened and the pump 20 operated to reduce the pressure in the furnace 17 to below 0.1 mm. of mercury. The taps 22 and 25 are opened to cause a gaseous mixture of hydrogen and the carbonyl to flow into the furnace 17, the taps 19 and 22 being adjusted to control the rate of flow of this gaseous mixture and the pressure within the furnace 17, this pressure being maintained at about 5 mm. of mercury and the rate of flow of the gaseous mixture being about 15 litre/min. It will be understood that although the carbonyls of the transition elements in Group VI are solids at N.T.P. their vapor pressure is sufficient to provide the required quantity of gaseous carbonyl at the reduced pressure existing in the furnace 17. The gaseous mixture is allowed to flow into and through the furnace 17 for a period of at least 2 hours during which period the hydrogen reduces the carbonyl to the carbide which is deposited on the surface or surfaces of the die. After this the die 9 is cooled in a vacuum, and is subsequently removed from the furnace 17 and transferred to a high temperature furnace where it is heated to a temperature of 2000° C. to 2100° C. in a protective atmosphere, e.g., hydrogen, for a period of about 15 minutes and allowed to cool whilst the protective atmosphere is maintained in order to fire the carbide film on to the surface or surfaces of the die.

In the method of applying the carbide coating to the die cavity surface or surfaces by contacting the said surface or surfaces with a slurry of the metal carbide, a mixture of finely ground carbide powder and water is prepared. Upon agitation the fine powder will be suspended within the aqueous medium. The coating is applied by temporarily sealing the lower end of the die in such a manner as to plug the cavity or bore. The aqueous slurry is then introduced into the die cavity and agitated. The slurry may be additionally agitated prior to introduction to the die cavity in order to ensure a suitable suspension of the carbide powder. The solid particles will come out of the slurry and adhere to the surface or surfaces of the die cavity forming the desired film. Excess water and the temporary seal or plug are removed from the die cavity and the die is then loaded with the powder to be pressured. Protective gas such as argon, nitrogen, or hydrogen is introduced to the die cavity at the beginning of the pressing operation. As the hot pressing die assembly is brought up to the temperature for hot pressing the moisture is removed, and the car-
bide film is subjected to a temperature of at least about 2000° C. to fire the coating onto the said surface or surfaces. Alternatively, the contacting of the surface or surfaces of the die cavity with the aqueous-carbide mixture or slurry may be accomplished by painting or brushing the slurry on to the said surface or surfaces. Also, the desired carbide coating may be applied by first wetting the surface or surfaces of the die cavity with water in any convenient manner. Finely ground carbide powder is then dusted onto the wet surface. The so treated die is installed in the furnace, and the powder to be pressed is loaded into the die and subjected to the hot pressing operation.

The aqueous medium in these methods acts as an adhesive enabling the carbide to remain on the die until the powder to be pressed is introduced into the die. The powder when in the die supports the carbide material on the die wall and prevents it from flaking off as would occur when the die is not or adequately dried. Thus, it is apparent that the firing of the carbide coating can be accomplished either prior to the addition of the powder to the die or after the powder is introduced and during the hot pressing thereof.

FIGURES 4 and 5 illustrate a cylindrical graphite die 9 having a coating 27 of carbide in accordance with this invention, the thickness of this coating being exaggerated for the purpose of illustration. FIGURE 4 also shows two plungers 28 which may be hydraulically operated for the purpose of exerting a pressure on any powdered material placed in the die 9 for hot pressing to the shape of a rod.

A graphite die 9 having a carbide coating 27 in accordance with this invention is of particular, but not exclusive, application in the hot pressing of the diborides of titanium and zirconium. For example, when titanium diboride is hot pressed in a graphite die at a temperature of the order of 2000° C. there is a marked tendency for the titanium diboride to stick to the die with the result that the latter breaks before the pressing operation is completed, or the pressed body of titanium diboride breaks during cooling as a result of the differential contraction of the die and the pressed body. These difficulties are not encountered when the hot pressing operation is performed at a temperature below the order of 1700° C. but it is not possible to produce a satisfactory strong and dense body at such low temperatures. It is thought that titanium diboride and carbon have some mutual solubility at temperatures of the order of 2000° C. or above or that the effect may be due to small amounts of impurity, such as boron oxide (B₂O₃) which is not economic to remove from the titanium diboride powder. Whatever the reason for the sticking effect we have found that titanium diboride may be satisfactorily hot pressed at temperatures of the order of 2000° C. and above in a graphite die when the surface or surfaces of the wall or walls defining the cavity is or are coated with a film of the carbide of one of the transition elements in Groups IV, V and VI of the Periodic System, e.g., titanium carbide.

Reasonable hot pressed bodies of titanium diboride may be produced in graphite dies treated by the first method described above, i.e., by painting and firing, but it is extremely desirable, if not essential, that the painting and firing be repeated after each pressing operation.

Titanium diboride can be hot pressed at the highest temperatures normally used (about 2050° C.) in a die treated by any of the other methods described above without sticking occurring and a number of pressings (at least six) can be obtained from a given die without further treatment. As an example a powder of titanium diboride was hot-pressed in a cylindrical graphite die 9 such as illustrated in FIGURE 4 at a maximum temperature of 2050° C. and a maximum pressure of 1 ton/sq. in. on the plungers 28. The surface of the die 9 defining the cavity was coated with titanium carbide by the tetrachloride method described above. The resultant titanium diboride bar had a low porosity of the order of 6% by volume and a transverse rupture modulus of about 15 tons per sq. in. No sticking of the titanium diboride to the die 9 occurred and the surface of the die 9 defining the cavity was unimpaired and the die 9 was suitable for further operations.

The provision of a film of titanium carbide on the surface or surfaces of the wall or walls defining the die cavity is beneficial not only in the hot pressing of titanium diboride and the borides or diborides of the other transition elements in Groups IV, V and VI of the Periodic System but is also beneficial for the hot pressing of the carbides of such elements. For example, although sticking does not occur appreciably in the hot pressing of titanium carbide, the soft graphite dies do score in use and often have to be discarded for this reason alone. The treated dies, however, show no signs of scoring since the film is both hard and durable. This film is also helpful in minimizing die reaction in cases where the material being hot pressed reacts with the material of the die.

For example, oxide ceramics tend to react with the graphite of the die during pressing, but oxides are in general much less reactive towards titanium carbide.

It will be appreciated that although the invention has been specifically described with reference to producing a film of titanium carbide, vanadium carbide, zirconium carbide or molybdenum carbide on the surface or surfaces of the wall or walls of the die cavity it is not limited to the film being of one of these carbides as it is within the scope of the invention to provide such a film of a carbide of any one of the transition elements of Groups IV, V and VI of the Periodic System, namely, titanium, zirconium, hafnium, vanadium, niobium, tantalum and chromium, molybdenum and tungsten. At present, however, titanium tetrachloride is both the cheapest and most freely available material for producing a suitable film on the surface or surfaces of the wall or walls of the die cavity so that it is most economic to form the film from titanium carbide.

What I claim is:

1. A graphite die for use in a high temperature hot pressing process having disposed on the surfaces defining a die cavity a fired coating comprising a film of a carbide of a metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, said film containing no free metal.

2. A graphite die as in claim 1 wherein the fired coating is titanium carbide.

3. A graphite die as in claim 1 wherein the fired coating is zirconium carbide.

4. A graphite die as in claim 1 wherein the fired coating is molybdenum carbide.

5. A graphite die as in claim 1 wherein the fire coating is vanadium carbide.

References Cited by the Examiner

UNITED STATES PATENTS
2,860,075 11/58 Alexander et al. ------ 117—228 X

OTHER REFERENCES

RICHARD D. NEVIUS, Primary Examiner.