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METHOD OF PREPARING SINTERED ZIRCONIUM METAL FROM ITS HYDRIDES

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1 Claim. (Cl. 75—213)

This invention relates to the preparation of metal parts by powder metallurgical techniques. More particularly, it relates to the preparation of metal parts from the hydrides of metals such as zirconium by powder metallurgical techniques.

Zirconium is an interesting engineering material because of its high melting point (about 1860° C.) and its high resistance to most corrosive media. However, its use in the manufacture of machine parts or other types of parts by the normal casting and working methods is impractical and most difficult because of the high melting point of zirconium. Furthermore, since high purity zirconium metal is very expensive, machining losses are prohibitive. For this reason powder metallurgical techniques have been resorted to advantageously in the manufacture of such zirconium parts. In accordance with these techniques parts can be manufactured by pressing and sintering at temperatures considerably below the melting point of the material and furthermore there is practically no material lost. Since these techniques have been developed to a very considerable extent it is normally possible thereby to achieve high speed production of parts. In normal powder metallurgical techniques the material which is pressed and sintered is a comminuted or chemically prepared powder of the metal which is to be made into a part. Although this works quite satisfactorily with most metals, zirconium presents a distinct problem, for, although it is possible to produce the zirconium parts in this manner two major difficulties are encountered. One, finely divided zirconium is pyrophoric and therefore requires very skillful and careful handling if large losses are not to occur. Two, the metal from which the powdered zirconium is obtained by comminution is so ductile as to make it relatively difficult to prepare fine particles of a suitably high bulk density which combination is most desirable for obtaining the most dense materials by powder metallurgical techniques. Chemical means of preparing finely divided zirconium powder yield such a voluminous and low bulk density of the powder that an impractically large sized pressing die is required to contain the powder during pressing.

It is an object of this invention to provide a method of making zirconium or other metal parts which is not subject to the extreme fire hazard normally encountered in making zirconium or other pyrophoric metal parts by the normal powder metallurgical techniques.

It is a further object of this invention to provide an improved method by means of which it will be readily possible to make dense zirconium, zirconium alloy, and other metallic products by powder metallurgical techniques.

It has been found that these other objects and advantages which are incidental to its application can be obtained by using powdered hydride of zirconium or other metal as the starting material to form by powder metallurgical methods a compact metal article.

The zirconium hydride powder which is to be used for this purpose can be prepared, for example, by rendering

massive pieces of crystal bar zirconium friable by heat treatment in purified hydrogen. This can then be ground to form a powder which lies within the range of 6 to 10 microns in particle size. If desired, however, the average particle size of the hydride can be reduced to two microns since the hydrogen treated crystal bar is quite friable. The powder so formed can be handled in the air without danger of it igniting, contrasted with zirconium powder which is normally handled in the air only in especially moist condition or under a suitable organic liquid. The zirconium hydride powder may be compacted in the normal manner by being placed in a die and needs no binder nor any lubrication of the die wall. The compacting pressure, as is true in normal powder metallurgical work, varies somewhat with the characteristics of the particles and upon the shape and dimensions of the part and upon whether or not the pressure is to be exerted from both top and bottom. In practice it has been found that the zirconium hydride powder is equally as compressible as zirconium powder under the same pressing conditions and that the hydride compacts to approximately the same percentage of the density of zirconium hydride as does the zirconium powder compact to the density of zirconium. Furthermore, in actual operation it has been found that although the density of the compact itself increases steadily with the applied compacting pressure between 20 and 75 t. s. i. the application of pressures above approximately 50 t. s. i does not measurably affect the density of the compact in the sintered state.

The compact may then be sintered under vacuum conditions preferably at a temperature ranging from 1200 to 1300° C. and for periods of one to three hours. In the vacuum sintering of zirconium hydride compacts, in contrast with zirconium compacts, the pressure increases during the first half hour of the heating period. During this period hydrogen is being given off and the pressure may rise from a starting pressure of about 0.01 micron to more than 25 microns. This occurs while the compact is passing through the temperature range of about 500 to 900° C. The period of high pressure owing to the escape of hydrogen varies, of course, with the amount of hydride in the furnace. After the cooling period the charge is removed from the furnace and it has been found that the average sintered density obtained is the density of zirconium; i. e. 6.54 g./cc. The vacuum during this operation is preferably held within the range of 0.2 to 0.06 micron.

Another advantage of the process of this invention lies in the fact that the zirconium dihydride and the zirconium monohydride powder compacts attain the density of zirconium metal (6.54 g./cc.) at lower sintering temperatures and in shorter times than is possible with zirconium metal powder.

It has been found that the zirconium hydride compacts may also be sintered in an inert atmosphere such as argon but in such cases the density is not quite as high although it is sufficiently close to being considered practically identical averaging about 6.4 g./cc. as compared to 6.5 for the vacuum sintered material.

The zirconium hydride compacts can be sintered at a minimum temperature of about 1215° C. for a time of one hour as compared to about 1230° C. and a time of three hours for zirconium powder. This is of considerable importance in the case of a gas gettering metal such as zirconium. For the lower the temperature and the shorter the time necessary for accomplishing the sintering the less opportunity there is for the zirconium to dissolve additional oxygen. Example: a crystal bar of zirconium is made friable by heat treatment in purified hydrogen. The friable bar is then ground to obtain a zirconium hydride powder which lies within the range of 6 to 10 mi-

crons. This material is then introduced into a floating cylindrical die of a 0.789 diameter cavity. The massive die block containing the cavity was guided during the floating action by four vertical posts which pass through holes in its periphery, floated approximately ⅛" during the pressing of 6.5 g. of zirconium hydride to a thickness of 3/16". The compact so obtained is then vacuum sintered in a system operating in the pressure range of 0.20 to 0.04 micron. When a compacting pressure of 50 t. s. i. is used the density of the zirconium hydride compact is approximately 5.10 g./cc.

When this material is subsequently heated and sintered at a temperature of 1230° C for a period of one hour it achieves a density of 6.5 g./cc.

Although the description given above deals specifically with zirconium hydrides, the principal objective of making metal parts by using powdered metal hydride as the starting material to form compact articles of the metal by powder metallurgical methods can be attained equally well with other hydride forming metals than zirconium, since the hydrides are friable and since they can be decomposed to the metal under suitable and attainable conditions. Among other known hydride forming metals of high melting points of over 1700° C. there may be listed columbium, chromium, tantalum, thorium, vanadium. These may all be handled advantageously in accordance with the herein described method.

While the above description discloses preferred and practical embodiments of the method of preparing metallic parts from metallic hydrides it will be understood by those skilled in the art that the specific details described are by

way of illustration and are not to be construed as limiting the scope of the invention.

What is claimed is:

The process of producing zirconium metal of theoretical density which comprises heating zirconium metal in purified hydrogen to form zirconium hydride, comminuting the hydride to a powder having a particle size in the range 2 to 10 microns, compacting the powdered hydride at room temperature to a density approaching that of zirconium metal, relieving the compacting pressure and thereafter sintering the compacted hydride in an inert atmosphere at a temperature in the range 1215 to 1230° C. for a time sufficient to produce zirconium of theoretical density.

References Cited in the file of this patent

UNITED STATES PATENTS

2,107,279	Balke et al.	Feb. 8, 1938
2,254,549	Small	Sept. 2, 1941
2,393,906	Hensel et al.	Jan. 29, 1946

OTHER REFERENCES

Wulff: "Powder Metallurgy," pub. by the American Society for Metals, Cleveland, Ohio (1942), pp. 146 and 147 and 152.

Strauss, Jr.: "TiH Increases Compact Density," Steel, May 6, 1946, pp. 138 and 160.

Gibb, Jr.: "Compounds of Hydrogen With Metals and Metalloids," Journal of the Electrochemical Society, vol. 93, No. 5, May 1948, pp. 199–211, pages 208 and 209 relied upon.