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PROCESS FOR MAKING WORKABLE RUTHENIUM AND PRODUCT THEREOF

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This invention relates to the production of ruthenium metal products and, more particularly, to processes for improving the workability of ruthenium metal.

It is well known that even though ruthenium is a member of the platinum metals group, ruthenium differs greatly from other platinum group metals in that ruthenium produced by methods of the prior art is not characterized by the workability of platinum and palladium, or even that of rhodium and iridium. Ruthenium is a refractory metal normally produced as a powder by the reduction of a salt or compound of the element. When the metal is required in a consolidated form, the powder may be melted and cast or may be compacted and sintered by conventional powder-metallurgical techniques. When the former method for consolidation is used, the resultant metal is not readily workable. The few prior art reports of experimental working of ruthenium indicate that, at best, this metal could be worked only with great difficulty and that consistent success was not achieved even when very difficult and expensive methods were employed in preparing and working this metal. Illustrative of the failure of the past experimentors to produce readily workable ruthenium is the statement in the 1961 edition of the Rare Metals Handbook (Reinhold Publishing Corporation), on page 317, "Ruthenium and osmium have never been successfully worked."

The utilization of ruthenium has been greatly restricted by the lack of any process for producing readily workable ruthenium metal, although it is well known that ruthenium is advantageously characterized by a high degree of corrosion resistance and a high melting point, as well as by other potentially useful characteristics. Until now the metallurgical art has been in need of a process for producing ruthenium metal characterized by a commercially useful degree of workability suitable for production of ruthenium metal products and articles in order to more fully utilize the advantageous characteristics of ruthenium. Although many attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that ruthenium metal characterized by a high degree of workability hitherto unknown in the prior art can be produced by a new melting process.

It is an object of the present invention to provide a process for improving the workability of melted ruthenium metal.

Another object of the invention is to provide a readily workable ruthenium metal ingot produced by a new process.

The invention also contemplates providing new alloys of ruthenium.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates processes for improving the workability of ruthenium metal by subjecting molten ruthenium metal to permeation by a small amount of at least about 0.005% of a

permeating element selected from the group consisting of up to about 5% zinc, up to about 5% bismuth, up to about 5% cadmium, up to about 0.25% barium, up to about 0.25% germanium, up to about 0.25% hafnium, up to about 0.25% titanium, up to about 0.25% cerium, up to about 0.25% erbium, up to about 0.25% gadolinium, up to about 0.25% holmium, up to about 0.25% lanthanum, up to about 0.25% praseodymium, up to about 0.25% samarium, up to about 0.25% ytterbium, and up to about 0.25% yttrium. All percentages set forth herein are weight percentages based on weight of ruthenium metal. It is essential that the added element or elements be present while the ruthenium is molten so as to permeate the molten ruthenium. If added in the course of consolidating ruthenium powder by powder metallurgical techniques without subsequent melting, no satisfactory result (improvement in workability) is obtained. Ruthenium metal ingots produced by processes of the invention whereby molten ruthenium is permeated by zinc, cadmium, or bismuth are substantially devoid of these elements. When the aforementioned rare earth elements are used to perform the process of the invention, the process of the invention provides ingots of new melted single-phase ruthenium alloys containing a total of 0.005% to about 0.25% of these rare earth metals, i.e., cerium, erbium, gadolinium, holmium, lanthanum, praseodymium, samarium, ytterbium and yttrium, and characterized by improved workability.

In carrying the invention into practice, the workability of ruthenium metal is increased by melting it in the presence of small quantities of zinc, bismuth, cadmium, barium, germanium, hafnium, titanium and/or the aforementioned rare earth metals. Of the foregoing elements which can be the added or permeating element, it is advantageous to use zinc because it is relatively cheap, easy to obtain and readily volatilized. Improvement in workability is obtained with extremely small additions of any one or more of the aforementioned elements, such an extremely small addition being as little as 0.005%. For zinc, cadmium and bismuth, the range of amounts employed is about 0.005% to about 5%. For the other permeating elements, namely, barium, germanium, hafnium, titanium, cerium, erbium, gadolinium, holmium, lanthanum, praseodymium, samarium, ytterbium and yttrium, the range of amounts employed is about 0.005% to about 0.25%.

In producing ruthenium ingots in accordance with the invention and in further processing such ingots, one skilled in the metallurgical art should of course observe known practices for producing high quality ruthenium metal. Thus, the ruthenium metal used as the starting material for the process of the invention should be substantially devoid of, or at least low in, known detrimental contaminants. A typical ruthenium metal that is satisfactory for use as the starting material in producing ruthenium of improved workability in accordance with the invention is a powder produced by the hydrogen reduction of ruthenium ammonium chloride, which powder contains minor residual impurities in the following amounts:

	Percent
Palladium -----	0.001
Rhodium -----	0.004
Osmium -----	0.02
65 Gold -----	0.001
Iron -----	0.006
Nickel -----	0.0002
Lead -----	0.0003
Antimony -----	0.001
70 Tin -----	0.0005

The process of the invention is performed under non-

oxidizing conditions, as those skilled in the art will understand. An argon arc furnace, whereby ruthenium metal can be arc melted on a water-cooled hearth in an argon atmosphere using a nonconsumable electrode, has been found most satisfactory. It is desirable to use a ruthenium electrode in the argon arc furnace in place of the usual tungsten electrode in order to eliminate contamination of the ruthenium by tungsten. The argon atmosphere of the furnace should be gettered by melting a button of titanium in the furnace prior to use of the furnace for melting ruthenium in practicing the invention. Permeation of the molten ruthenium may be accomplished in vacuum. However, in the case of a vacuum furnace there are numerous complications, not the least of which is the contamination of the ruthenium from the crucible and the linings. The method of introduction of the permeating elements is critical in the sense that the element must permeate the molten ruthenium. The most satisfactory method of introducing the permeating element that we have found is the method described in the following examples. The ruthenium metal is kept molten for a sufficient length of time to provide that the permeating element permeate the molten metal. For instance, in carrying out the process of the invention, it is sufficient to heat the molten ruthenium metal in the presence of the permeating element in an argon arc furnace to a temperature above its melting point, that is, above about 2310° C., for such a period that the melt is seen to be quiescent and free from the evolution of gas.

The mechanism by which the added element improves the workability is not properly understood and in fact workability is improved even when the permeating element is wholly removed from the ruthenium and the resulting ruthenium ingot is substantially devoid of the permeating element. For example, when ruthenium ingots are produced using zinc, cadmium, or bismuth as the permeating element these elements are wholly removed in the course of the process of the invention and the resulting ingots obtained upon cooling the permeated melt to room temperature are substantially devoid of these elements. By "wholly removed" and "substantially devoid of" it is meant that the amount remaining or present, if any, is less than one part per million, as determined by mass spectrographic analysis of the ruthenium metal. The rare earth elements used as the permeating elements in processes of the invention are not completely removed from the ruthenium and the invention also provides new melted alloys consisting essentially of about 0.005% to about 0.25% of metal selected from the group consisting of cerium, erbium, gadolinium, holmium, lanthanum, praseodymium, samarium, ytterbium and yttrium with the balance essentially ruthenium. The ruthenium alloys produced in accordance with the invention are necessarily single phase alloys. Dual or multiple phase alloys would be brittle and hence not workable.

Ruthenium metal processed in accordance with the invention can be readily worked by hot forging, swaging and/or rolling provided the metal is reheated at 1450° C. or above between successive reductions and then the temperature during the early stages of working does not drop below about 1200° C.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example I

Ruthenium metal powder prepared by hydrogen reduction of ruthenium ammonium chloride and containing minor residual impurities in amounts such as are set forth in the foregoing analysis was used as the starting material. Zinc, in an amount equal to 0.5% of the ruthenium metal, was used as the permeating element. Forty grams of ruthenium metal powder were consolidated by hydrostatic pressure of 20 long tons per square inch into a compact and a piece of zinc weighing about 0.2 gram was

pressed into the compact. The compact was then placed in an argon arc melting furnace with the added element at the bottom and close to the water-cooled hearth. The ruthenium was then subjected to permeation by the zinc by heating the compact to a temperature above its melting point (about 2310° C.) and holding it at that temperature until the molten surface of the melt was quiescent and free from the evolution of gas. Thereafter, the melt was solidified into an ingot and the ingot was then cooled and turned over and the melting process was repeated without further addition of zinc. The resulting ingot was found to be readily workable.

Example II

A ruthenium metal ingot was produced as set forth in Example I except that 0.02 gram of cerium was used as the permeating element instead of 0.2 gram of zinc. The resulting ingot was found to be readily workable.

Rare earth elements with which improvements in workability have been obtained include cerium, erbium, gadolinium, holmium, lanthanum, praseodymium, samarium, ytterbium and yttrium. The improved workability that is characteristic of ruthenium metal produced in accordance with the invention is not obtained by using neodymium and dysprosium as permeating elements in attempting to perform the process of the invention. Neodymium and dysprosium are not permeating elements of the invention.

Ruthenium metal processed in accordance with the present invention is characterized by improved workability as compared with ruthenium metal processed only by prior art methods. The improved workability of ruthenium metal processed in accordance with the present invention is evidenced by the following results showing that the readily workable ruthenium metal ingots of the invention can be hot-worked to a reduction in thickness of over 90%. Ruthenium metal ingots of about one inch diameter and of 0.3 inch to 0.4 inch maximum thickness were produced by arc melting ruthenium powder in argon. At least one ingot was made using each of the permeating elements of the invention individually. Workability of the ingots was assessed by hot rolling the ingots, using a re-heat temperature of 1450° C. and a reduction per pass of 0.01 inch. Ingots that has been subjected during melting to permeation by one of any of the permeating elements of the invention were readily workable and were successfully reduced to 0.02 inch thickness, a reduction in thickness of between 93% and 95%. Some ingots of zinc-permeated ruthenium were rolled further to a thickness of 0.005 inch, a reduction in thickness of over 98%. Ruthenium metal ingots produced without being subjected to permeation in accordance with the invention, but otherwise produced and hot-worked by the same methods used in producing and hot-working ingots of the invention, had poor workability and cracked and fell to pieces during the first three to ten passes, i.e., after reductions of between 7% and 25%.

The present invention is particularly applicable to the production of ruthenium metal ingots for use as workpieces in forging, rolling, extruding and other metal working operations. Ruthenium metal ingots of the invention can be worked into products such as bars, strip, sheet, etc., or worked directly into useful articles of manufacture such as, inter alia, electrical contacts and crucibles.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for improving the workability of ruthenium metal comprising permeating molten ruthenium

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metal in a non-oxidizing atmosphere with a small amount of at least about 0.005% of a permeating element selected from the group consisting of up to about 5% zinc, up to about 5% bismuth, up to about 5% cadmium, up to about 0.25% barium, up to about 0.25% germanium, up to about 0.25% hafnium, up to about 0.25% titanium, up to about 0.25% cerium, up to about 0.25% erbium, up to about 0.25% gadolinium, up to about 0.25% holmium, up to about 0.25% lanthanum, up to about 0.25% praseodymium, up to about 0.25% samarium, up to about 0.25% ytterbium, and up to about 0.25% yttrium, maintaining the ruthenium in a molten condition until the molten ruthenium is substantially quiescent and free from gas evolution and thereafter solidifying the molten ruthenium.

2. A process as set forth in claim 1 wherein cerium in an amount of about 0.005% to about 0.25% is the permeating element.

3. A process as set forth in claim 1 wherein zinc in an amount of about 0.005% to about 5% is the permeating element and wherein the ruthenium metal is kept molten until the zinc is wholly removed from the ruthenium.

4. A readily workable ruthenium ingot made of a ruthenium alloy consisting essentially of about 0.005% to about 0.25% of metal selected from the group consisting of cerium, erbium, gadolinium, holmium, lanthanum, praseodymium, samarium, ytterbium and yttrium with the balance essentially ruthenium, said alloy being a single-phase alloy and said ingot being characterized by improved workability such that the ingot can be worked to a reduction in thickness of at least 90%.

5. A single-phase alloy consisting essentially of about 0.005% to about 0.25% of metal selected from the group consisting of cerium, erbium, gadolinium, holmium, lan-

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thanum, praseodymium, samarium, ytterbium and yttrium with the balance essentially ruthenium.

6. A process for improving the workability of ruthenium metal comprising melting ruthenium metal in a non-oxidizing atmosphere and treating the ruthenium by contacting the ruthenium with at least about 0.005% of a permeating element selected from the group consisting of up to about 5% zinc, up to about 5% bismuth, up to about 5% cadmium, up to about 0.25% barium, up to about 0.25% germanium, up to about 0.25% hafnium, up to about 0.25% titanium, up to about 0.25% cerium, up to about 0.25% erbium, up to about 0.25% gadolinium, up to about 0.25% holmium, up to about 0.25% lanthanum, up to about 0.25% praseodymium, up to about 0.25% samarium, up to about 0.25% ytterbium, and up to about 0.25% yttrium to cause said element to permeate the molten ruthenium, holding the thus treated molten ruthenium containing said permeating element until the molten ruthenium is substantially quiescent and free from gas evolution and thereafter solidifying the molten ruthenium.

7. A process as set forth in claim 6 wherein cerium in an amount of about 0.005% to about 0.25% is the permeating element.

8. A process as set forth in claim 6 wherein zinc in an amount of about 0.005% to about 5% is the permeating element and wherein the ruthenium metal is kept molten until the zinc is wholly removed from the ruthenium.

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