United States Patent

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[54] METHOD FOR PRODUCING ULTRA-HIGH PURITY METAL
10 Claims, 2 Drawing Figs.

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[51] Int. Cl. C22d 7/00, C22b 51/00, C22b 51/20
[50] Field of Search 75/10, 65, 84; 219/121

[56] References Cited

UNITED STATES PATENTS

2,960,331	11/1960	Hanks	75/65
2,809,905	10/1957	Davis	75/10
3,086,856	4/1963	Siebertz	75/10
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1,010,307	11/1965	Great Britain	219/121

OTHER REFERENCES

Inert Gas Replaces EB Welding Vacuum, Welding Engineer P. 52 (July, 1962).

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ABSTRACT: For electron-beam zone-refining of metal, at least one zone-refining pass is conducted in a hydrogen atmosphere at a system pressure sufficiently low to prevent formation of a hydrogen arc-discharge. This is followed by at least one zone refining pass in a high vacuum. The resulting metal is extremely pure.

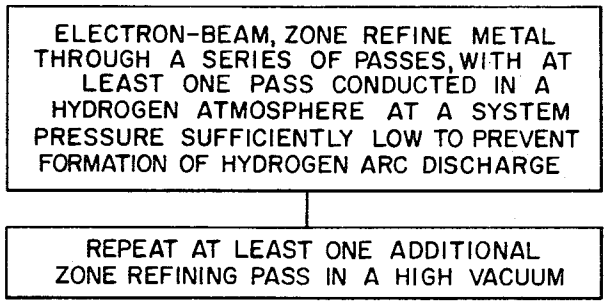


FIG. 1.

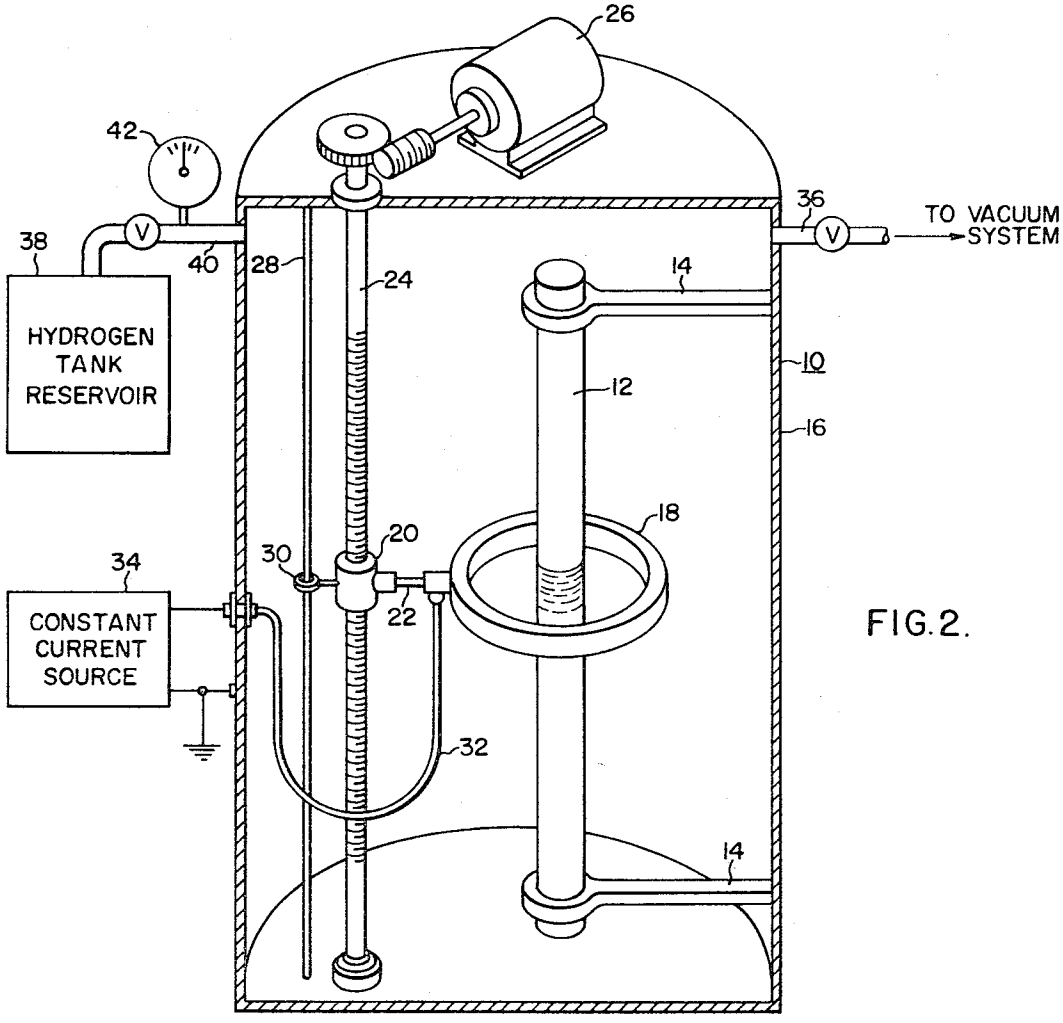


FIG. 2.

WITNESSES

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METHOD FOR PRODUCING ULTRA-HIGH PURITY METAL

BACKGROUND OF THE INVENTION

This invention relates to refining of metals and, more particularly, to an improved electron-beam, zone-refining method for producing extremely pure metal.

Electron-beam zone-refining of metals, particularly of the refractory type, is well known and is described in U.S. Pat. No. 2,809,905 dated Oct. 15, 1957 to Davis et al. In U.S. Pat. No. 3,218,154 dated Nov. 16, 1965 to Sell et al. is disclosed an improved method for such electron-beam zone-refining wherein a so-called compact of metal is zone refined, in order to improve the purity of the refined metal. In U.S. Pat. No. 3,338,706 dated Aug. 29, 1967 to Morcom et al. is described an electron-beam, zone-refining process for making alloys of refractory metals, wherein a plurality of rods of different materials are simultaneously zone refined to produce the refractory metal alloy.

All of the foregoing processes conduct the zone refining in a vacuum since the presence of a gas will normally result in creating a gas discharge between the cathode and the metal anode. The creation of a gas discharge renders the zone-refining process ineffective.

In the general state of the art regarding purification of refractory metals, it has long been known to sinter such materials in a hydrogen atmosphere using either a separate-heated furnace or a self-resistance heating technique wherein electrodes are connected to the ends of a compact or a so-called green ingot, and a current of several 1,000 amperes is passed therethrough in order to cause the individual particles of the compact to sinter into a unitary body.

SUMMARY OF THE INVENTION

It is the general object of the present invention to provide an improved method for electron-beam, zone-refining metal in order to increase the purity of the metal.

It is another object to provide an improved method for electron-beam, zone-refining refractory metal, and particularly niobium and tantalum, in order that the residual resistance ratio of such metal, which is an indicia of purity, is greatly increased.

The foregoing objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by modifying the usual electron-beam, zone-refining process so that at least one zone-refining pass is conducted in a hydrogen atmosphere at a system pressure which is sufficiently low to prevent the establishment of a hydrogen arc discharge. This pass in the hydrogen atmosphere is followed by at least one additional zone-refining pass in a high vacuum, in order to remove any residual gas from the metal undergoing processing.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention, reference should be had to the accompanying drawings wherein:

FIG. 1 is a flow diagram illustrating the basic steps of the present method; and

FIG. 2 is a diagrammatic view of a zone refining apparatus as may be used to practice the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present method can be used in zone refining any metals or alloys thereof, as described in the foregoing patents. The present method is particularly effective, however, for use in refining refractory metals, such as niobium and tantalum. With specific reference to the form of the invention illustrated in the drawings, the basic method of electron-beam zone-refining is as set forth in the foregoing U.S. patents wherein a self-sustaining, elongated mass of metal is refined by bombarding a limited length portion of the elongated mass with a high-intensity, electron beam in order to melt same. The elongated mass and electron beam are moved relative to one another at a predetermined rate to sequentially melt adjacent limited length portions of the mass, with melted portions of the mass solidifying after bombardment. In accordance with the present invention, and as shown in the flow diagram of FIG. 1, at least one of the zone refining passes is conducted in a hydrogen atmosphere at a system pressure which is sufficiently low to prevent formation of a hydrogen arc discharge. This pass in the hydrogen atmosphere is followed by at least one additional zone refining pass in a high vacuum, in order to remove any residual gas from the metal.

With reference to the zone-refining apparatus **10**, as shown in FIG. **2**, the self-sustaining, elongated metal mass **12**, which is undergoing zone refining, can be formed of a preformed rod or a compacted and presintered mass or rod of metal, or a rod of refractory metal which has been completely sintered and then swaged to a desired diameter. As a specific example, the elongated rod **12** undergoing refining is formed of niobium or tantalum having a length of 3 inches to 18 inches and a diameter of about 0.3 inch, for example. This rod **12** is supported at its ends by suitable supports **14**, which in turn are affixed within the controlled-atmosphere chamber formed by the enclosure **16**. The cathode **18** of the zone refining apparatus is affixed to a threaded sleeve **20** by means of an insulating connecting member **22**. The cathode **18** is moved relative to the rod **12** undergoing refining by rotation of the threaded rod **24**, which is driven by a motor **26** geared to one end of the threaded rod **24**. A guide rod **28** receives an eyelet **30** which serves to maintain the cathode **18** in proper orientation about the rod **12** being processed. Current is applied to the cathode **18** by means of a lead-in member **32** which is connected to a constant current source **34** as generally described in U.S. Pat. No. 3,165,571 dated Jan. 12, 1965 to Grimes. The atmosphere within the chamber is controlled and is either a vacuum, obtained by connection through conduit **36** to a vacuum system, or a controlled pressure of hydrogen as regulated by the hydrogen tank reservoir **38** and associated valved-conduit **40** and gauge **42**.

In the general operation of the apparatus **10** as shown in FIG. **2**, the cathode **18** is moved relative to the rod **12** undergoing treatment in order to bombard the rod **12**, which acts as the the anode, with a high-intensity electron beam, to melt a limited length portion of the rod. In this apparatus, the cathode is moved relative to the stationary rod **12** in order to sequentially melt adjacent limited length portions of the rod, with previously melted portions of the rod solidifying after bombardment. The impurities in the metals are more soluble in the molten material than in the solid material and as a result, the impurities are carried to an end or ends of the rod **12** undergoing treatment, which can be ultimately removed from the remaining "pure" rod portion. In the usual zone refining processes, more than one pass is utilized to purify the metal.

In accordance with the present invention, it has been found that by conducting at least one of the zone-refining passes at a relatively low hydrogen pressure, which is not adequate to support a hydrogen arc discharge, and then following this "-hydrogen atmosphere pass" with at least one pass in a high vacuum, the resulting metal is extremely pure. It would normally be expected that any appreciable amount of hydrogen in the system would result in a hydrogen arc discharge, which would impair the operation of the zone-refining process. This has not been found to be the case, however, and with the particular equipment as illustrated, it has been found that the zone refining pass in the hydrogen atmosphere should be at a pressure, as measured at the gauge **42**, no greater than about 5×10^{13} torr. As a matter of practicality, it is desirable to maintain the hydrogen pressure at from about 1×10^{14} torr to about 3×10^{15} torr. This assures that there will be no tendency to form a hydrogen arc discharge at the higher pressure end of this range and at a pressure lower than that specified, the effectiveness of the purification process is decreased.

Prior to conducting the pass or passes in the hydrogen atmosphere as indicated, it is preferred to conduct two or more passes in a high vacuum, such as a vacuum of less than 5×10^{17} torr. Also, it is preferred to conduct at least two zone refining passes in the hydrogen atmosphere as indicated, thereafter followed by at least two additional zone-refining passes, and preferably three of such passes, in a high vacuum.

The present process has been found to be most effective in purifying niobium and tantalum. The resulting metal is so pure that the impurities can be effectively measured only by what is known in the art as the "residual resistance ratio" of the metal. This is the electrical resistance of the metal measured at a temperature of 273° K. divided by the electrical resistance of the metal measured at a temperature 4.2° K. In the case of niobium, the control sample which was zone refined only in vacuum displayed a residual resistance ratio of approximately 300. When the metal was purified utilizing the hydrogen atmosphere as specified hereinbefore, followed by additional zone refining in vacuum, the residual resistance ratio was greater than 10,000. In the case of tantalum, the residual resistance ratio utilizing vacuum only in the zone refining was approximately 500, but when tantalum was purified in accordance with the present method, the residual resistance ratio was greater than 10,000.

While both dry hydrogen and moist hydrogen can be used in the controlled atmosphere step, it is preferred to use moist hydrogen having a dew point of about 20 to 25° C. Also, the zone-refining apparatus as shown in FIG. 1 could readily be modified to move the rod 12 relative to a stationary cathode.

It will be recognized that the objects of the invention have been achieved by providing an improved method for electron-beam zone-refining metal, and particularly niobium and tantalum, in order to obtain extremely pure material, the purity of which is represented by a high residual resistance ratio.

While preferred examples have been illustrated and described, it is to be particularly understood that the invention is not limited thereto or thereby.

What is claimed is:

1. The method of purifying a self-sustaining elongated mass of metal by repeated electron-beam, zone-refining passes, wherein during each pass a limited length portion of said elongated mass is bombarded by a high-intensity electron beam to melt same, and the elongated mass and electron beam are moved relative to one another at a predetermined rate to sequentially melt adjacent limited length portions of said mass, with melted portions of said mass solidifying after bombardment, which method comprises:

a. conducting at least one of said zone-refining passes in a hydrogen atmosphere at a system pressure which is sufficiently low to prevent the establishment of a hydrogen discharge,

b. thereafter repeating at least one additional zone-refining pass in a higher vacuum to remove any residual gas.

2. The method as specified in claim 1, wherein said hydrogen atmosphere is at a system pressure of no greater than about 5×10^{13} torr.

3. The method as specified in claim 1, wherein said hydrogen atmosphere is at a system pressure of from about 1×10^{14} torr to about 3×10^{14} torr.

4. The method as specified in claim 1, wherein prior to said zone-refining pass in said hydrogen atmosphere, at least one of said zone-refining passes is conducted in a high vacuum.

5. The method as specified in claim 1, wherein there are conducted at least two of said passes in a hydrogen atmosphere.

6. The method as specified in claim 1, wherein said metal mass is refractory metal.

7. The method as specified in claim 6, wherein said refractory metal mass is niobium or tantalum.

8. The method as specified in claim 6, wherein said hydrogen atmosphere has a dew point temperature of about 20 to 25° C.

9. The method of purifying a self-sustaining elongated mass of metal by repeated electron-beam, zone-refining passes in an electron-beam, zone-refining system, wherein during each pass a limited length portion of said elongated mass is bombarded by a high-intensity electron beam to melt same, and the elongated mass and electron beam are moved relative to one another at a predetermined rate to sequentially melt adjacent limited length portions of said mass, with melted portions of said mass solidifying after bombardment, which method comprises:

a. conducting at least one of said zone-refining passes in a hydrogen atmosphere introduced from a separate hydrogen reservoir into said system at a system pressure no greater than about 5×10^{13} torr which is sufficiently low to prevent the establishment of a hydrogen discharge,

b. thereafter repeating at least one additional zone-refining pass in a higher vacuum to remove any residual gas.

10. The method as specified in claim 9, wherein said hydrogen atmosphere is at a system pressure of from about 1×10^{14} torr to about 3×10^{15} torr.