Aug. 29, 1967 W. R. MORCOM ET AL 3,338,706

METAL PROCESSING METHOD AND RESULTING PRODUCT

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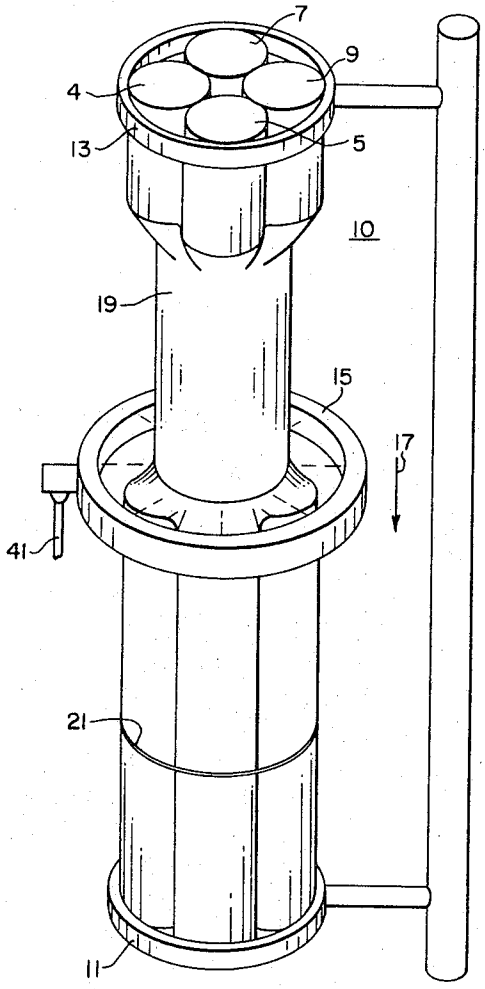
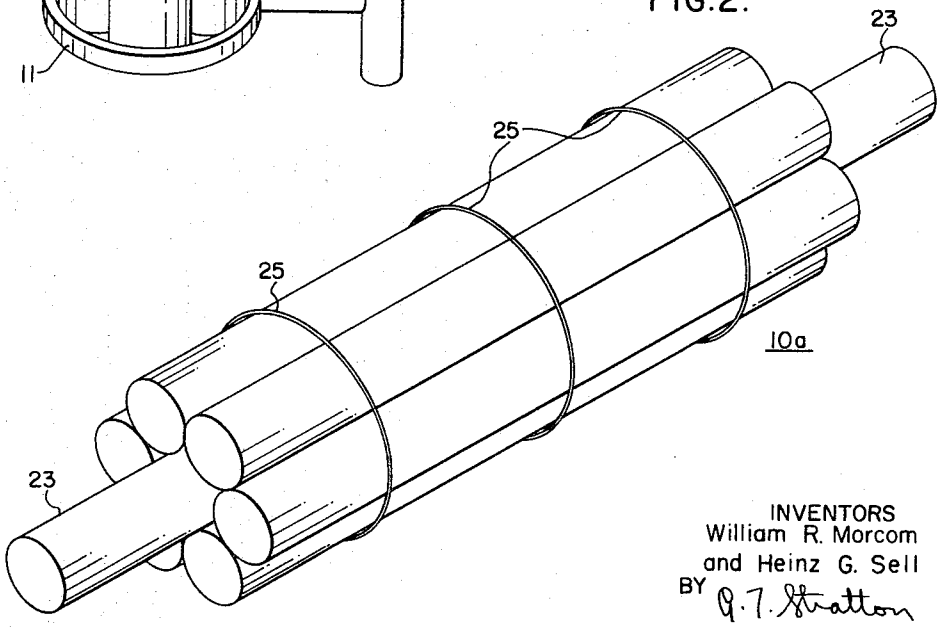


FIG.1.

FIG.2.

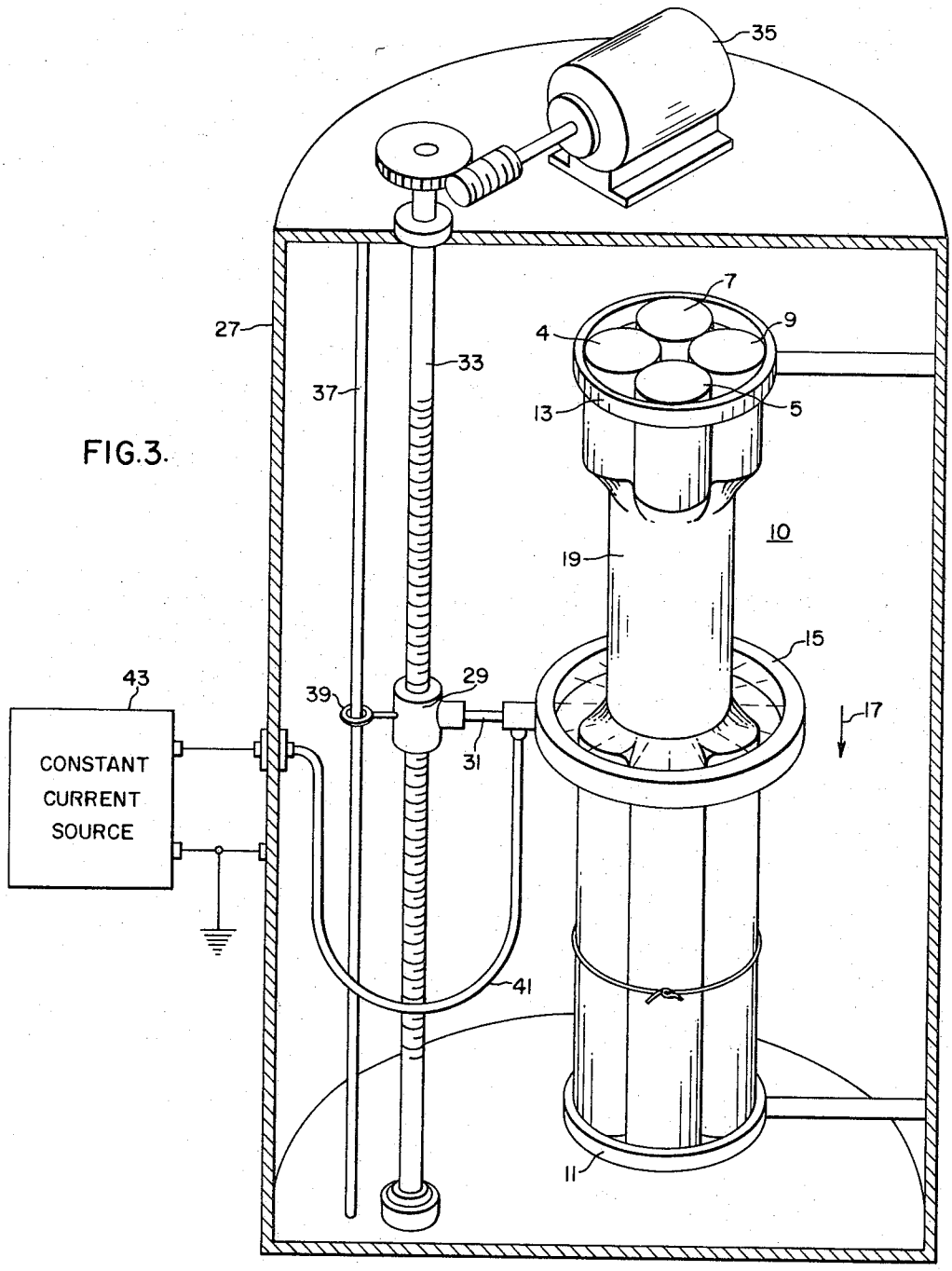


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METAL PROCESSING METHOD AND RESULTING PRODUCT

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FIG.3.



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METAL PROCESSING METHOD AND RESULTING PRODUCT

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ABSTRACT OF THE DISCLOSURE

To form very pure alloys comprising refractory metals, rods of pure metal of the alloy constituents are bundled together. The bundled rods are then melted by a zone-refining process to form the homogeneous alloy.

This invention generally relates to the formation of alloys and, more particularly, to the formation of very pure alloys.

Many difficulties are encountered in forming very pure alloys, such as obtaining the ingredients in a practical form prior to alloying them together. Particularly in the case of refractory metals, the ingredients must be powdered and pressed into a compact, prior to alloying by sintering. Another difficulty is controlling the nominal composition of the alloy. Usually this is accomplished by weighing the ingredients, but the alloy may be contaminated by the crucible in which the constituents are prepared. In additions, the melting point of the alloy may be so high that no presently known crucible can withstand the temperature. Degassing and purifying the ingredients of the alloy sometime presents difficulties. Volatile impurities in the interior of the alloy must be allowed to escape. The alloy must be produced in a commercially usable form.

It is, therefore, an object of this invention to provide a simple and precise method of forming an alloy, as well as the product prepared by the method.

Another object of this invention is to provide a method of forming an alloy directly from constituents as they can be obtained in commercially available form.

A further object of this invention is to provide a method of forming an alloy, the composition of which can be determined simply and precisely.

An additional object of this invention is to provide a simple method of forming a refractory metal alloy, which method does not require a crucible.

Still another object of this invention is to provide a method of forming an alloy in which volatile impurities are provided with an escape path.

Yet another object of this invention is to provide a method of forming an alloy directly into a commercially usable form.

Briefly, these and other objects are accomplished by placing together in a bundle, rods containing the constituents of the alloy in the desired, predetermined proportions, and then zone melting the bundle into a single homogeneous rod of the alloy. The zone melting is accomplished by slowly traversing the bundle along its length with a melting device.

The novel features which are believed to be characteristic of the invention, both as to its organization and method of operation, together with further objects and advantages thereof, will be better understood from the following detailed description considered in connection with the accompanying drawing in which an embodiment of the invention is illustrated by way of example. It is to be expressly understood, however, that the accompanying drawing is for the purpose of illustration and description only, and is not intended as a definition of the limits of the invention.

The accompanying drawings include,

FIG. 1 which shows a bundle of rods illustrating one embodiment of the invention;

FIG. 2 which shows another embodiment of the invention having one rod longer than the others; and

FIG. 3 which shows a bundle of rods supported within an electron beam, zone-refining apparatus.

Referring now to FIG. 1, a bundle **10** is formed by placing together elongated refractory metal members **4**, **5**, **7** and **9**. The bundle **10** is held together and supported proximate its ends by a suitable supporting means **11** and **13**. Individual refractory metal members may be supported at intermediate points as necessary. One method of intermediate support is to hold the members together with a wire **21**. As used in the apparatus as shown in FIG. 3, the cathode **15** traverses the bundle **10** in the direction of the arrow **17** and supplies an electron beam of sufficient energy to melt the section of the bundle **1** directly under the cathode **15**. Other suitable forms of melting energy such as thermal radiation and R.F. heating may be employed. The operation is performed in a vacuum in the case of electron-beam melting. The width of the melted section is limited by the energy and the intensity of the electron bombardment and is easily controlled.

Referring now to FIG. 2, another embodiment **10*a*** of the bundle is shown supported at each end of extra long member **23**. The other members are held to member **23** by means of wires **25**. These wires may or may not be included in the final alloy. If they are to be included, their effect on the final composition may be minimized by using very thin wires or wires made of the same material as the bulk of the alloy. The tieing wires may be eliminated from the final alloy by making the wires of a volatile substance which vaporizes due to the intense heat or in the case of forming low melting temperature metals, the wires may be made of refractory materials which do not melt at the temperatures involved. A suitable electron beam apparatus is generally disclosed by Davis et al. in U.S. Patent No. 2,809,905.

FIG. 3 shows an apparatus which is adapted to carry out the present method. The bundle **10** is supported by end support means **11** and **13** which are in turn supported within a vacuum chamber **27**. The cathode **15** is affixed to a threaded sleeve **29** by an insulative connecting member **31**. The threads on the inside of the threaded sleeve **29** match the threads on threaded bar **33** which is inserted therethrough. The cathode is moved relative to the bundle **10** by rotating the threaded bar **33** by means of a motor **35** which is geared to one end of the bar **33**. In order to guide the cathode relative to the bundle **10**, a guide rod **37** is inserted through an eye **39** extending from the threaded sleeve **29**. Currrent is supplied to the cathode **15** by means of lead **41** which has enough slack to allow the cathode **15** to traverse the bundle **10**. The electron beam current is provided by a constant current source **43**. The current source used in this application has special regulation characteristics to prevent arcing of the electron beam. A constant current source suitable for this application is disclosed by William M. Grimes, Jr. in U.S. Patent No. 3,165,571.

In performing the electron-beam, zone-melting operation, the molten material is retained within the melted section. The melted section is narrow enough so that the natural forces in the material, such as surface tension, cohesive, and adhesive forces prevent the melted material from running out. A vertical orientation of bundle **10** aids in retaining the molten material. However, under circumstances where the natural forces are sufficient, a nonvertical orientation may be employed.

As the electron beam traverses either up or down the axis of the bundle **10**, the narrow molten section also progresses. The portion of the bundle **10** on the traversed

side of the cathode 17 forms a single bar 19. The portion of bundle 10 on the other side of cathode 15 is still comprised of separate members. The member with the lowest melting point melts first and runs into the spaces between the other members and wets them. This wetting causes an initial alloy to be formed on the surface of the other members. These alloys are comprised of material from the first melting member and the surface material on each of the other members. As the melting continues, all of the elongated bars are melted to form a single alloy comprising the entire cross section of bundle 10. The composite alloy usually has a melting point considerably less than the highest melting point found among the individual members.

The volatile impurities, bubbles and gases contained inside each member escape through the spaces between the members. As the melting progresses the high temperatures cause the volatile impurities to form bubbles inside the members. These bubbles along with the bubbles and gases already present are forced to the surface of the relatively small members and escape through the spacings therebetween. This added purifying action is in addition to the inherent purifying action noted in the aforementioned patent to Davis et al.

As an example, the above described method has been successfully used to form alloys of tungsten and rhenium, such as 75% tungsten and 25% rhenium by weight. In making such an alloy, three tungsten rods 4, 5 and 7 and one rhenium rod 9 are bundled together with a tungsten wire 21 and supported vertically. An electron source traverses the bundle at a rate of 2 mm. per minute. The length of each of the members 4, 5, 7 and 9 is approximately 9 inches, and each is approximately 0.12 inch in diameter.

Any of the following combinations may be alloyed by the present method. The metals comprising these alloys will normally be present in such relative amounts as to be within their solubility limits.

W-Mo	Ta-Nb-Hf
W-Re	Ta-Nb-Mo
W-V	Nb-Hf
W-Nb	Nb-Mo
W-Ta-Mo	Nb-Th
W-Nb-Mo	Nb-Ti
W-Ta-Hf	Nb-V
W-Ta-Nb	Mo-Re
W-Re-Os	Mo-Hf
W-Nb-V	Mo-V
W-Mo-Nb	Pd-Ir
Ta-Nb	Pd-Ir-Os
Ta-Mo	

This list is not intended to be all inclusive as the instant method is applicable to other metals.

Normally all the constituents of the desired alloy will be provided among the members of bundle 10. Each constituent may be provided by a single member, or may be provided by several members. Many of the present commercial purifying and refining techniques involve rod-forms having dimensions practicable for the instant method from which the members may be selected. The rods may be conveniently weighed or measured before alloying them to determine the composition of the alloy to be formed.

The final proportions of each constituent contributed by the members must be within its solubility limits with respect to the other constituents. Otherwise the bar portion 19 will not be homogeneous and grains of the overabundant constituents will be present. If the overabundance of a particular constituent is slight, however, the excess will be carried along with the impurities in the molten section.

The chemical stability and vapor pressure of the molten material at the temperatures involved are important considerations. The instant method is particularly applicable

to refractory metal processing where the melting temperature exceeds 1600° C. Chemical activity may be decreased by removing the surrounding atmosphere. A low vapor pressure environment also enhances outgassing and removal of volatile impurities.

In other embodiments of the invention, such as the induction melting technique, a vacuum is not required. In such case, however, chemical activity is suppressed by replacing the atmosphere with an inert or non-reacting gas, such as a noble gas. The presence of a surrounding atmosphere also decreases the vaporization of materials having low vapor pressures. In special instances the surrounding atmosphere may contribute to the composition of the final alloy.

In the prefrered embodiment, the melting is accomplished by an electron beam. It is to be understood that any melting means of the appropriate geometry will suffice. Induction heating, a plasma ion beam, or hot ring devices, may be employed in the operation of this invention.

Broadly summarizing the present method, the alloy constituents are bundled together as a plurality of elongated members, at least some of which members have a different composition, with the composite composition of the bundled members corresponding to the predetermined composition desired in the alloy. The bundle is supported under non-reactive conditions, which constitutes a vacuum when an electron-beam, zone-refining process is used to effect the alloying. Limited sections of the bundle are then progressively melted to form a progressing, homogeneous melt. Each previously melted section of the bundle is permitted to solidify as the next succeeding section of the bundle is melted. The progressive melting of the bundle and solidifying of the melt is continued until a predetermined desired length of the supported bundle is melted, solidified, and thus formed into the alloy.

It will be recognized that the objects of the invention have been achieved by providing a simple and precise method for forming an alloy, as well as the resulting product. The method is particularly adapted for forming alloys of refractory metals, wherein the alloy constituents in the form as used are readily available. In forming the alloy, any volatile impurities have an easy escape path, thereby resulting in an increased degree of purity.

While the invention has been shown in but one form, it will be apparent to those skilled in the art that it is not so limited, but is susceptible of various changes and modifications without departing from the spirit thereof.

We claim as our invention:

1. The method of forming a refractory alloy, which method comprises:
   (a) bundling together a plurality of elongated members, at least some of which are of different composition, and which members have a composite composition corresponding to the predetermined composition desired in said alloy;
   (b) supporting said bundle in a vacuum;
   (c) progressively melting by electron-beam, zone-refining limited sections of said bundle to form a progressing homogeneous melt of all members of said bundle;
   (d) permitting each melted limited section of said bundle to solidify after melting; and
   (e) continuing to progressively melt and then solidify said bundle until a predetermined length of said bundle is formed into said alloy.

2. The method of forming an alloy of predetermined composition, which method comprises:
   (a) bundling together into a bundle a plurality of elongated members at least some of which are of different composition, said bundle having a composite composition, through every cross section to be formed into said alloy, which corresponds to the predetermined composition desired in said alloy;

(b) supporting said bundle under non-reactive conditions;

(c) progressively melting a limited section of all members of said bundle to form a homogeneous melt;

(d) permitting each melted limited section of said bundle to solidify after melting; and

(e) continuing to progressively melt and then solidify said bundle until a predetermined length of said bundle is formed into said alloy.

3. The method as specified in claim 2, wherein said elongated members are maintained in bundles formed by a retaining wrapping means which is formed of a constituent of said alloy.

4. The method of forming an alloy from refractory materials which have negligible vapor pressures at the melting temperature of said alloy, which method comprises the steps of:

(a) placing together in a bundle elongated members having compositions which substantially include the constituents of said alloy;

(b) supporting said bundle within a non-reactive environment; and

(c) traversing said bundle along its length dimension with a melting means by relative motion between the length dimension of said bundle and said melting means to melt a limited section of all members of said bundle adjacent to said melting means, whereby the bundle is progressively melted and then solidified to form said alloy.

5. A method of forming an alloy of a predetermined composition from refractory materials which has negligible vapor pressure at the melting temperature of such alloy, which method comprises the steps of:

(a) placing together in a bundle elongated members having compositions which include the constituents of said alloy, the proportion of each constituent included among said elements being within its solubility limit with respect to the other constituents;

(b) supporting said bundle proximate its ends in a substantially vertical position;

(c) establishing around said bundle a non-reacting environment; and

(d) establishing a relative motion between said bundle and a melting means to progressively melt a limited section of all members of said bundle to form a molten alloy which is held within said limited section by the natural forces within said molten alloy, and which thereafter progressively solidifies to form said alloy.

6. A method of forming and purifying an alloy from refractory materials which has negligible vapor pressure at the temperature required to melt said alloy, said refractory materials having impurities more soluble in the molten state of the alloy than in the solid state of the alloy, which method comprises the steps of:

(a) placing together in a bundle elongated members having compositions which include the constituents of said alloy, the proportions of each of the constituents among said members being within their solubility limits with respect to the other constituents;

(b) supporting said bundle proximate its ends in a substantial vertical position;

(c) establishing a non-reacting environment around said bundle; and

(d) traversing said bundle along its length dimension with a melting means by a relative motion between said bundle and said melting means to progressively melt a limited section of all members of said bundle and form a molten alloy which is prevented from running out of said limited section by the natural forces within said molten alloy and which thereafter progressively solidifies.

7. A method of forming an alloy of predetermined composition from refractory materials, which alloy has negligible vapor pressure at its melting temperature, which method comprises the steps of:

(a) forming a bundle of elements having compositions which include the constituents of said alloy, the proportions of each constituent being within the solubility limit of that constituent with respect to the other constituents;

(b) supporting said bundle proximate its ends in a substantially vertical position;

(c) establishing around said bundle a substantial vacuum;

(d) bombarding a limited section of said bundle with an electron beam having sufficient energy so as to melt all of said limited sections;

(e) melting all of said limited section by means of said electron beam to form a molten alloy of the material within said limited section which is prevented from running out by the natural forces within said molten alloy; and

(f) continuously moving said bundle and said electron beam relative to another along the length dimension of said bundle, thereby progressively melting and solidifying limited sections of said bundle to form said alloy.

8. A pure refractory metal alloy, said refractory metal alloy having been formed by the method which comprises:

(a) bundling together a plurality of elongated members, at least some of which are of different composition, and which members have a composite composition corresponding to the predetermined composition desired in said alloy;

(b) supporting said bundle in a vacuum;

(c) progressively melting by electron-beam, zone-refining limited sections of all members of said bundle to form a progressing homogeneous melt;

(d) permitting each melted limited section of said bundle to solidify after melting; and

(e) continuing to progressively melt and then solidify said bundle until a predetermined length of said bundle is formed into said alloy.

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