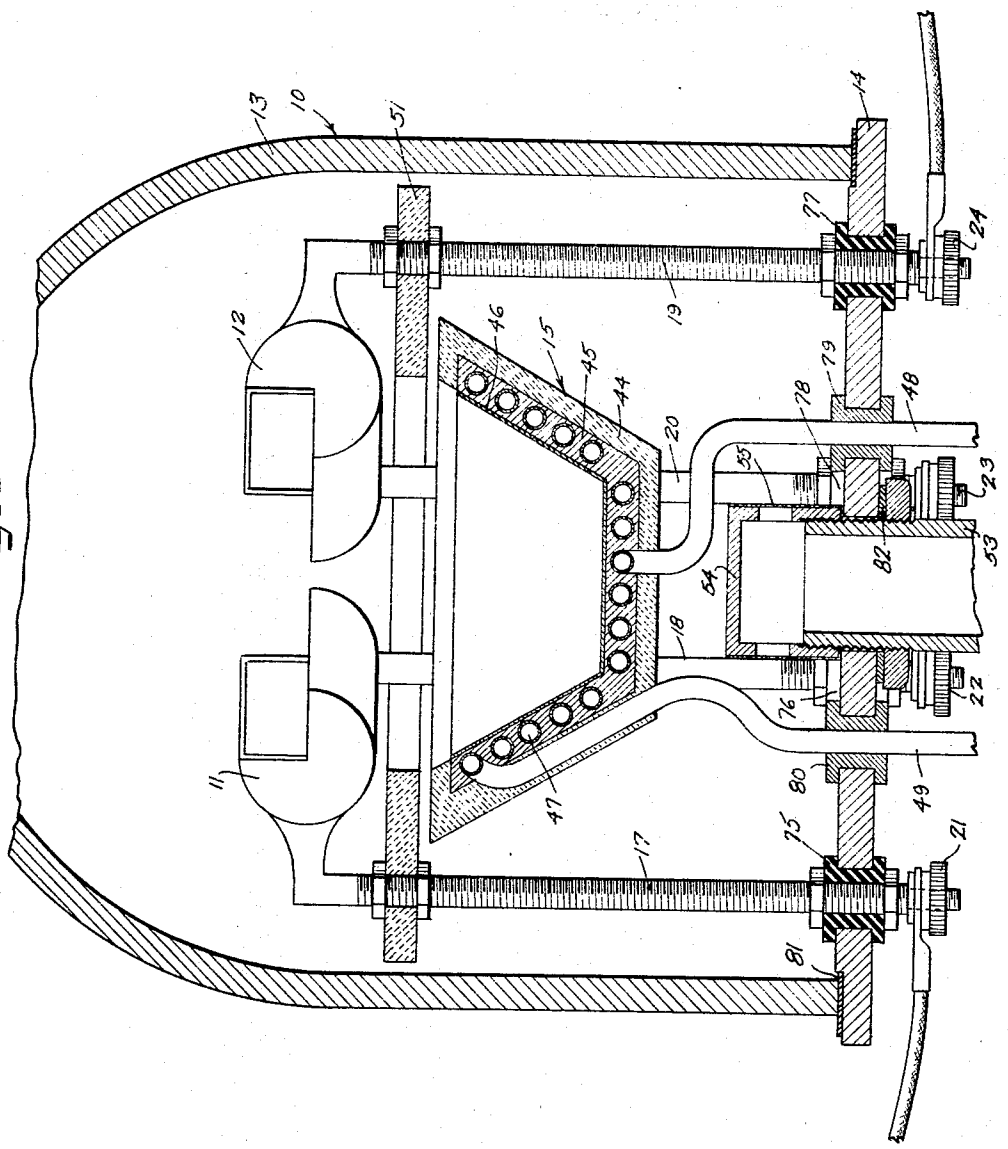
Nov. 22, 1966 J. K. HAUSNER 3,287,108

METHODS AND APPARATUS FOR PRODUCING ALLOYS

Filed Jan. 7, 1963 3 Sheets-Sheet 1

Fig. 1



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Filed Jan. 7, 1963 3 Sheets-Sheet 2

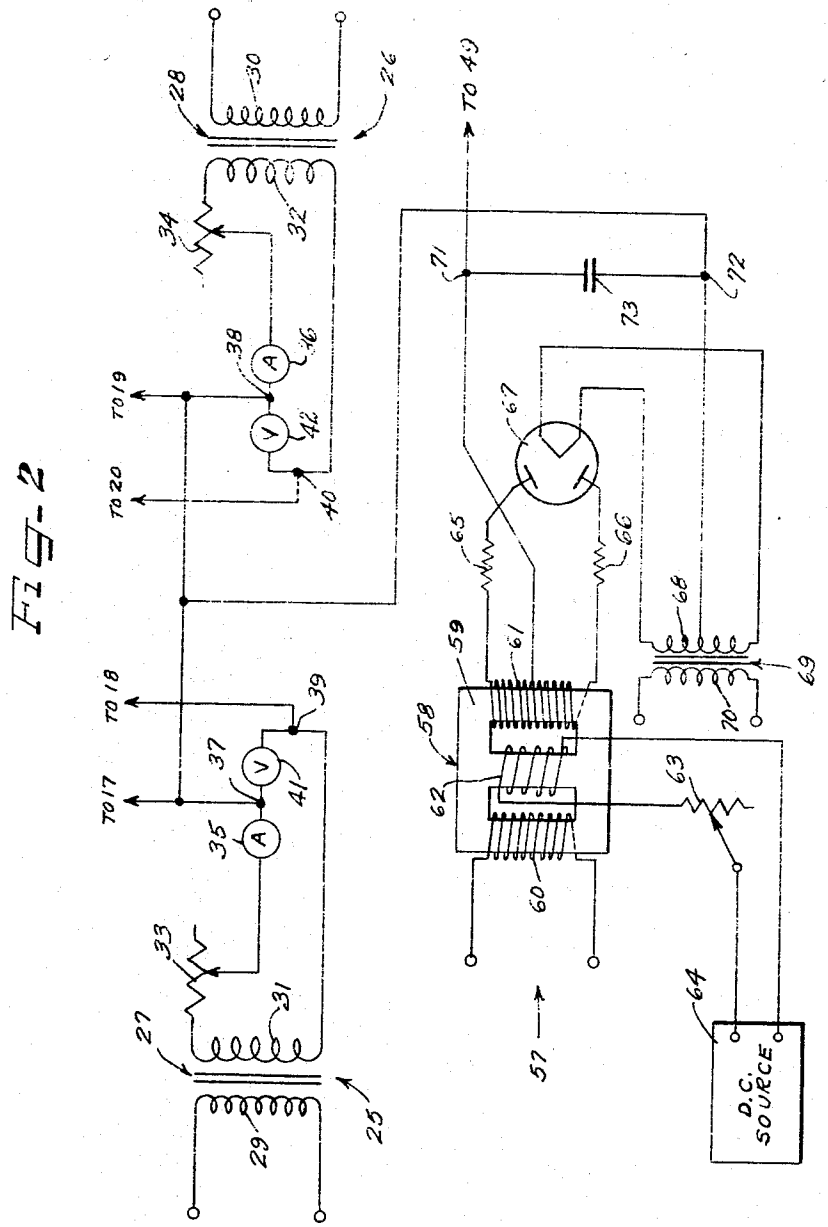


FIG-2

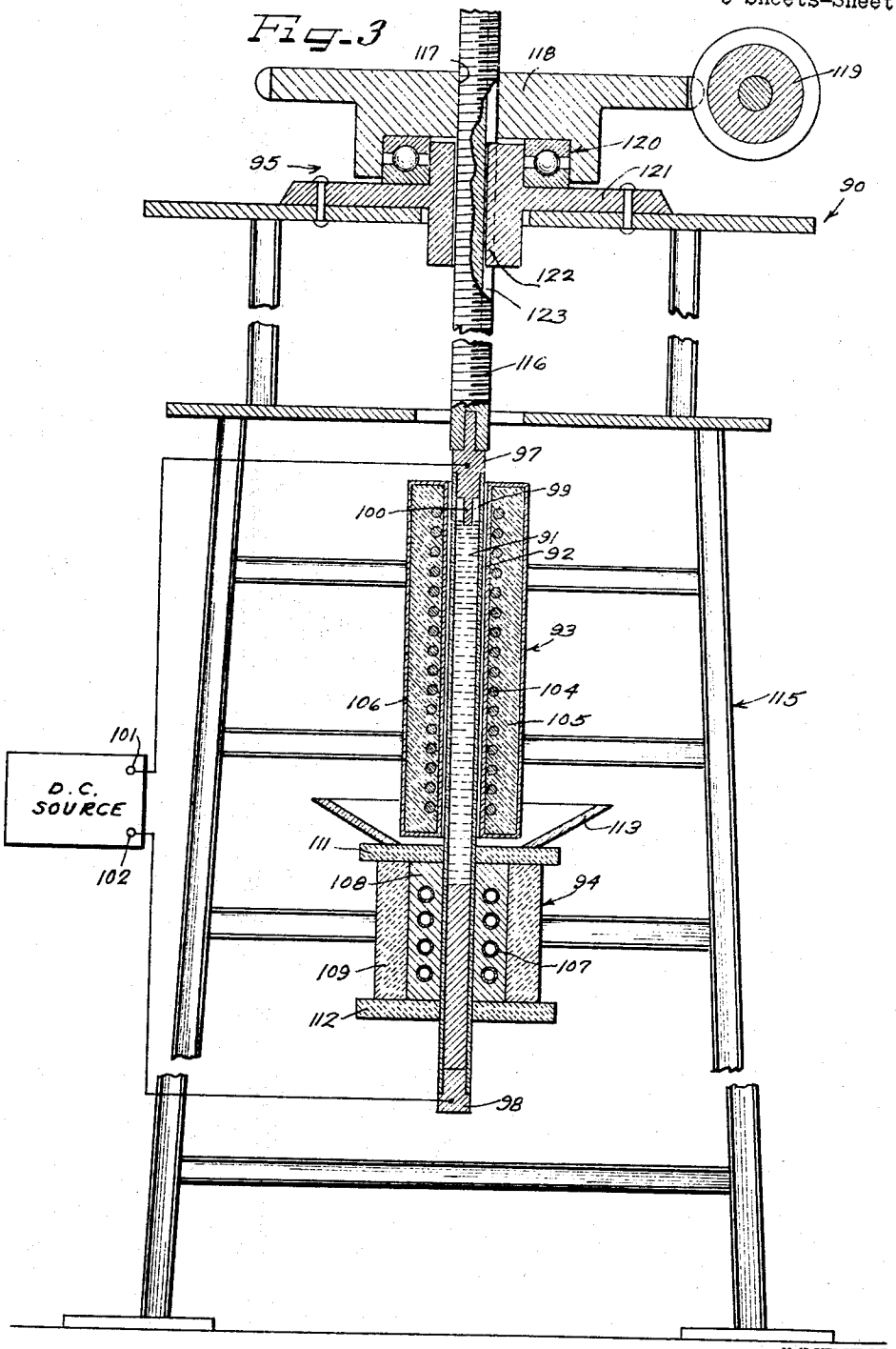
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METHODS AND APPARATUS FOR PRODUCING ALLOYS

Filed Jan. 7, 1963 3 Sheets-Sheet 3

Fig. 3



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United States Patent Office 3,287,108 Patented Nov. 22, 1966

3,287,108

METHODS AND APPARATUS FOR PRODUCING ALLOYS

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Filed Jan. 7, 1963, Ser. No. 249,744
14 Claims. (Cl. 75—10)

This invention relates to methods and apparatus for producing alloys and more particularly to crystallized semi-conductor alloys having an extremely high and uniform purity, such as employed in thermoelectric applications.

Quite rigid requirements are imposed in the production of alloys for thermoelectric applications. In such applications, junctions may be provided wherein a donator element of a junction emits electrons which are absorbed by an acceptor element. By heating the junction, electricity may be generated. In the alternative, current may be passed in one direction through the junction to cause an absorption of heat or cooling, or current may be passed through the junction in the opposite direction to cause heating thereof. To obtain high efficiency, it is essenital that the elements have a high electric conductivity while having a heat conductivity which is as low as possible. These results can be obtained with certain crystallized semi-conductor alloy materials having a high and uniform purity, which may be doped with very small amounts of certain materials. By way of example, alloys of tellurium with bismuth, antimony or selenium are suitable for many applications.

This invention was evolved with the object of producing such semi-conductor alloys with a high degree of purity and uniformity, although various features of the invention may be used in other applications.

An important feature of the invention relates to the use of a high voltage electrostatic field between a region within a vacuum chamber wherein metals are vaporized and another region wherein the metals are condensed and alloyed. With the proper application of the high voltage field, it is possible to produce particles of the alloys in exact quantities and absolute uniformity.

Another important feature of the invention relates to the casting of an alloy so produced into a rod and the heating and cooling of the rod while passing a current therethrough to remove impurities and to produce a crystallized portion of extremely high purity and uniformity. The current produces an electrolytic action causing impurities to move to one end or the other of the rod, leaving the central portion in a purified state.

This invention contemplates other and more specific objects, features and advantages which will become more fully apparent from the following detailed description taken in conjunction with the accompanying drawings which illustrate preferred embodiments and in which:

FIGURE 1 is a partially diagrammatic view illustrating an alloying unit constructed according to the principles of this invention;

FIGURE 2 is a circuit diagram of electrical apparatus for the unit of FIGURE 1; and

FIGURE 3 is another partially diagrammatic view showing a purification and crystallization apparatus usable in conjunction with the apparatus of FIGURE 1.

Reference numeral **10** generally designates apparatus for the alloying of metals, constructed according to the principles of this invention. In the general operation of the apparatus **10**, metals to be alloyed are placed in smelting pots **11** and **12** within a vacuum chamber defined by a dome **13** on a base plate **14**. The metals are heated in the smelting pots **11** and **12** to be vaporized, the vaporized metals being then condensed and alloyed in a condensing

pot unit **15**. Thereafter, the alloyed metals are cast into rods and treated further by the apparatus illustrated in FIGURE 3, to crystallize the same and to remove impurities.

The smelting pots **11** and **12** are heated by passage of electric current therethrough and are constructed of thin tungsten sheets formed into horizontal hollow cylinders having upper portions cut out for receiving the metal.

A first pair of vertical support and current-carrying rods **17** and **18** have upper ends mechanically and electrically connected to opposite ends of the pot **11** while a second pair of rods **19** and **20** have upper ends connected to opposite ends of the pot **12**. Electrical terminals **21–24** on the lower ends of rods **17–20** are provided for connection to sources of heating current, two A.C. sources **25** and **26** being provided.

The sources **25** and **26** comprise transformers **27** and **28** having primary windings **29** and **30** for connection to A.C. supply lines and secondary windings **31** and **32** having ends connected through rheostats **33** and **34** and through ammeters **35** and **36** to output terminals **37** and **38**, with the other ends of the secondary windings being connected to output terminals **39** and **40**. Volt meters **41** and **42** may be connected between the output terminals.

Output terminals **37** and **39** are connected to the rod terminals **17** and **18** while output terminals **38** and **40** are connected to rod terminals **19** and **20**, the smelting pots **11** and **12** being heated by the currents to a temperature at which the metals are vaporized.

The condensing pot unit **15** comprises an outer shell **44**, preferably of a ceramic material, with an inner cup **45** therein which is preferably of copper or other heat-conductive material. The inner surface of the cup **45** is preferably coated or plated with a layer **46** of chromium or other hard material. A cooling coil **47** of hollow tubular material is embedded in the copper cup **45**. End portions **48** and **49** of the coil **47** extend downwardly through the base plate **14** and serve to support the condensing pot unit **15**. Portions **48** and **49** are connected to a suitable source of recirculating cooling fluid, not shown.

An annular plate **51** of porcelain or the like is preferably supported on the rods **17–20**, the outer edge thereof being adjacent the inside surface of the dome **13**, and the inner edge thereof being adjacent the upper inside edge of the condensing pot unit **15**.

For evacuation of the space within the dome **13**, a pipe **53** is connected to a vacuum pump, not shown, and extends upwardly through the base plate with a cap **54** on the upper end thereof having screen-covered side openings **55**.

After placing the metals to be alloyed in the smelting pots **11** and **12**, the space within the dome is evacuated and the smelting pots are then heated by the current from sources **25** and **26** to vaporize the metals which are then condensed in the condensing pot unit **15**, cooled by the cooling coil **47**.

An important feature of the invention is in the application of a high potential electrostatic field between the smelting pots **11** and **12** and the condensing pot unit **15**. With this field, an electro-vaporization operation is obtained which greatly increases the uniformity of molecular conditions of the vaporized alloys and makes it possible to produce the particles of the desired alloys in exact quantity and absolute uniformity. This is of course extremely important in the production of semi-conductor alloys for thermo-electric and similar applications.

To produce the high potential field, a high voltage source **57** is provided which comprises a transformer **58** having a three-legged core **59** with a primary winding **60** on one leg, a high voltage center-tapped secondary winding **61** on the second leg and a control winding **62** on the third leg. The primary winding **60** is connected

to an A.C. supply while the control winding **62** is connected through a rheostat **63** to a D.C. source **64**, the rheostat **63** being adjusted to control the degree of saturation of the third leg of the core to thereby control the voltage across the secondary **61**.

The ends of the high voltage secondary winding **61** are connected through current-limiting resistors **65** and **66** to the plates of a full wave rectifier tube **67** having a filament connected to a center-tapped secondary winding **68** of a filament transformer **69** having a primary winding **70** connected to an A.C. supply source.

The center taps of the windings **61** and **68** are connected to negative and positive output terminals **71** and **72**, a high voltage filter capacitor **73** being connected therebetween. The negative output terminal **71** is connected to the condensing pot unit through end portion **49** of the cooling coil **47** thereof, while the positive output terminal **72** is connected to the rods **17** and **19** so as to be connected to the smelting pots **11** and **12**.

The base plate **14** is preferably of metal and insulating sleeves **75**, **76**, **77**, **78**, **79** and **80** are provided where the rods **17**, **18**, **19** and **20** and portions **48** and **49** pass through the base plate. These sleeves **75–80** provide the necessary insulation for the application of the high voltage, and also define vacuum seals. Additional sealing members **81** and **82** are provided for the dome **13** and the pipe **53**.

The alloy condensed in the pot unit **15** of FIGURE 1 is preferably cast in rods and then treated by apparatus generally designated by reference numeral **90** in FIGURE 3.

In particular, the alloy is cast in a rod **91** within a tube **92**, preferably a quartz tube, which is placed in a vertical position and then lowered to pass first through a smelting zone within a heating unit **93** and then through a low temperature or deep freeze zone within a cooling unit **94**, the movement being controlled by a mechanism **95**.

An important feature of the invention is in the flow of current through the alloy during the heating and cooling treatment. As soon as the alloy starts to melt, this current causes electrolysis to take place and all impurities start to move either downwardly or upwardly toward one end or the other of the tube **92**, the direction of movement being determined by the chemical group of the impurity. When the alloy then reaches the cooling zone, it is crystallized into solid crystals of extremely high purity, except at the upper and lower end portions of the rod which then contain the impurities. In some cases, an improvement in results might be obtained by repeating the process. In most cases, however, only one treatment is required which is of considerable advantage over prior art systems wherein the crystallization process must be repeated many times.

To apply the current through the rod **91**, a pair of contacts **97** and **98** are secured to the upper and lower ends of the quartz tube **92**, preferably with a hermetic seal. An expansion space **99** may be provided between the upper contact **97** and the alloy **91** and, to insure electrical contact, a pin **100** projects downwardly from the lower end of contact **97** into the alloy.

Contacts **97** and **98** are connected through suitable flexible cables to terminals **101** and **102** of a D.C. source, as diagrammatically illustrated.

The heating unit **93** comprises a coil of wire **104**, preferably Nichrome wire, surrounded by an insulating sleeve **105** of asbestos or the like, the assembly being disposed in a suitable cover or casing **106**.

The cooling unit **94** comprises a coil **107** of hollow tubular material, embedded in a supporting sleeve **108** of heat-transmitting material, preferably sintered copper, sleeve **108** being enclosed by a sleeve **109** of insulating material such as asbestos.

To oppose flow of heat to the cooling unit **94** from the heating unit **93** and from the external space, a pair of cover rings **111** and **112** are disposed at the upper and lower ends of the cooling unit **94**. Rings **111** and **112** are preferably of a ceramic material. In addition, a frusto-conical reflector plate **113** is secured to the ring **111** in surrounding relation to the lower end of the heating unit **93**, to provide a shield against direct radiation from the heating unit.

The heating and cooling units **93** and **94** are supported in a suitable framework **115** which also supports the lowering machanism **95**. Mechanism **95** comprises a threaded rod **116** removably secured at its lower end to the upper contact member **97**. Rod **116** is threaded through an internally threaded opening **117** in a worm gear **118** driven by a worm **119** which is driven by a suitable drive, not shown. The worm gear **118** is supported through a bearing assembly **120** on a support member **121** secured to the upper end of the framework **115**. Support member **121** has a central opening through which the rod **116** extends and carries a key **122** extending into a keyway **123** on the rod **116** to prevent rotation of the rod **116**.

It may be noted that the vertical distance from the upper end of the heating unit to the lower end of the mechanism **95** and the distance from the lower end of the cooling unit to the base of the framework **115**, should be greater than the length of the tube **92** so as to permit insertion and removal of the tube **92**.

With the methods and apparatus as above described, it is possible to produce alloys of high purity and particularly crystallized semi-conductor alloys such as, for example, alloys of tellurium with bismuth, antimony or selenium. It may be noted that although the exact reasons for the improved results are not known with absolute certainty, it is believed that in the vaporization and condensing step of the process, the application of the high voltage field causes the charging of individual particles of the vaporized metals to reduce the particles of each metal to a very small size and to then bring such particles into intimate association as they condense in the condensing pot. Then in the purification and crystallization steps of the process, the passage of the electric current through the alloy causes an electrolytic action and movement of impurities either in the direction of a current or in the opposite direction, depending upon the chemical group of the impurity.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the novel concepts of this invention.

I claim as my invention:

1. In a method of producing alloys, the steps of separately heating and vaporizing a plurality of metals to be alloyed within a common vacuum chamber, and condensing and alloying the vaporized metals in a cooled condensing region while applying a high voltage electrostatic field between the vaporization and condensing regions.

2. In a method of producing crystallized semi-conductor alloys, the steps of separately heating and vaporizing a plurality of metals to be alloyed within a common vacuum chamber, condensing and alloying the vaporized metals in a cooled condensing region while applying a high voltage electrostatic field between the vaporization and condensing regions, casting the condensed alloy into rods, heating and then cooling the rods while passing an electric current longitudinally through the rods to cause impurities to move to one end or the other while leaving the central portion in a crystallized purified state.

3. In apparatus for producing alloys, means defining a vacuum chamber, smelting means in said chamber for heating a plurality of metals to vaporization temperatures, condensing means within said chamber for condensation of the vaporized metals therein, and means for applying a high voltage electrostatic field between said smelting means and said condensing means.

4. In a method of producing crystallized alloys, the steps of separately heating and vaporizing a plurality of metals to be alloyed within a common vacuum chamber, condensing and alloying the vaporized metal in a cooled condensing region while applying a high voltage electrostatic field between the vaporization and condensing regions, subsequently heating the condensed alloy, and then cooling and crystallizing the alloy.

5. In apparatus for purifying and crystallizing alloys, a tube for receiving a rod of unpurified alloy, an electrical heating coil arranged for receiving said tube and for heating the alloy to a high temperature, a cooling coil axially aligned with said heating coil for receiving said tube and cooling and crystallizing the alloy, and means for passing a current through said rod while it is disposed in said heating coil.

6. In a method of producing crystallized semi-conductor alloys, the steps of separately heating and vaporizing a plurality of metals to be alloyed within a common vacuum chamber, condensing and alloying the vaporized metals in a cooled condensing region, casting the condensed alloy into rods, heating and then cooling the rods while passing an electric current longitudinally through the rods to cause impurities to move to one end or the other while leaving the central portion in a crystallized purified state.

7. In apparatus for producing alloys, means defining a vacuum chamber, electrically heated smelting means in said chamber for heating a plurality of metals to vaporization temperatures, condensing means within said chamber for condensing the vaporized metals therein, a plurality of heating current sources, first conductor means extending from said current sources into said vacuum chamber and connected to said smelting means, second conductor means extending from said condensing means to a point outside said chamber, means insulating said first and second conductor means from each other, and a high voltage source connected between said first and second conductor means.

8. In apparatus for producing alloys, means defining a vacuum chamber, a plurality of smelting pots in said chamber for receiving a plurality of metals to be alloyed, means for passing an electric current through said pots to heat the metals to vaporization temperatures, a condensing pot in said vacuum chamber, means for applying a high voltage electrostatic field between said condensing pot and said smelting pots, means for receiving alloys condensed in said condensing pots, means for heating the alloy in said receiving means, and means for passing a unidirectional electric current through the heated alloy in said receiving means to cause impurities to move in one direction by electrolytic action.

9. In apparatus for purifying alloys, a tube for receiving a rod of unpurified alloy, heating means arranged to receive and surround said tube to heat the alloy therein, cooling means aligned with said heating means and arranged to receive and surround said tube to cool the alloy therein, means for slowly moving said tube through said heating means and thence through said cooling means, and means for passing a unidirectional electric current through said rod while disposed in said heating means.

10. In apparatus for producing alloys, means defining a vacuum chamber, a plurality of smelting pots in said chamber for receiving a plurality of metals to be alloyed, means for passing electric current through said smelting pots to heat the metals to vaporization temperatures, a condensing pot in said vacuum chamber, and means for applying a high voltage electrostatic field between said condensing pot and said smelting pots.

11. In apparatus for producing alloys, means defining a vacuum chamber, electrically heated smelting means in said chamber for heating a plurality of metals to vaporization temperatures, condensing means within said chamber for condensing the vaporized metals therein, a plurality of heating current sources, first conductor means extending from said current sources into said vacuum chamber and connected to said smelting means, second conductor means extending from said condensing means to a point outside said chamber, means insulating said first and second conductor means from each other, a high voltage source connected between said first and second conductor means, and means for separately regulating the currents applied from said plurality of heating current sources.

12. In apparatus for purifying and crystallizing alloys, a hollow tube of insulating material for receiving a rod of unpurified alloy, a pair of contacts on the opposite ends of said tube for making electrical contact with the unpurified alloy therein, means for heating the alloy within said tube, and means for connecting said contacts to a D.C. source to pass a current longitudinally through the alloy in said rod while heating the alloy.

13. In apparatus for producing alloys, means defining a vacuum chamber, electrically heated smelting means in said chamber for heating a plurality of metals to vaporization temperatures, condensing means within said chamber for condensing the vaporized metals therein, a plurality of heating current sources, first conductor means extending from said current sources into said vacuum chamber and connected to said smelting means, second conductor means extending from said condensing means to a point outside said chamber, means insulating said first and second conductor means from each other, a high voltage source connected between said first and second conductor means, and means for regulating the voltage of said high voltage source.

14. In apparatus for purifying alloys, a tube for receiving a rod of unpurified alloy, heating means for receiving said tube and heating the alloy therein to a high temperature, and means for passing a unidirectional current longitudinally through the alloy in said rod to electrolytically cause movement of impurities to one end or the other of the rod, said tube having a greater volume than the volume of said unpurified alloy placed therein, thereby providing an expansion chamber.

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