Nov. 26, 1957 J. S. BALLANTINE 2,814,560

APPARATUS AND PROCESS FOR MELTING MATERIAL OF HIGH MELTING POINT

Filed April 23, 1954

Fig. 1.

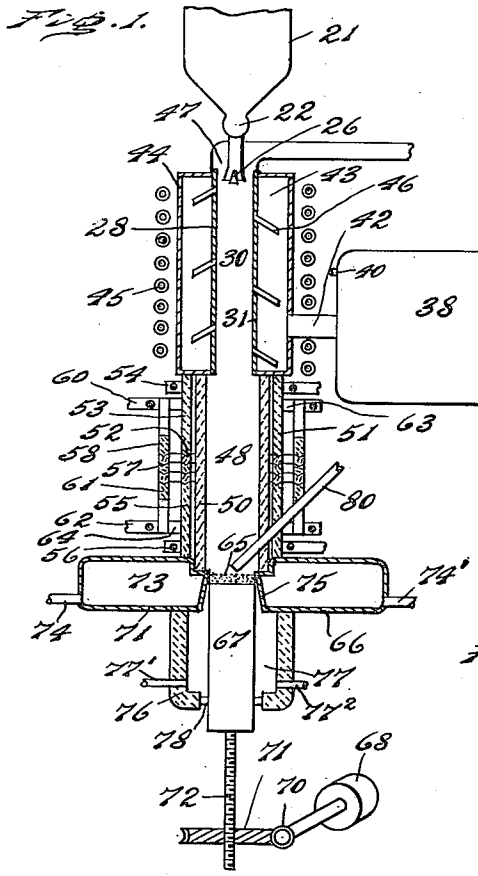


Fig. 3.

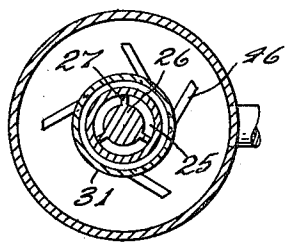


Fig. 2.

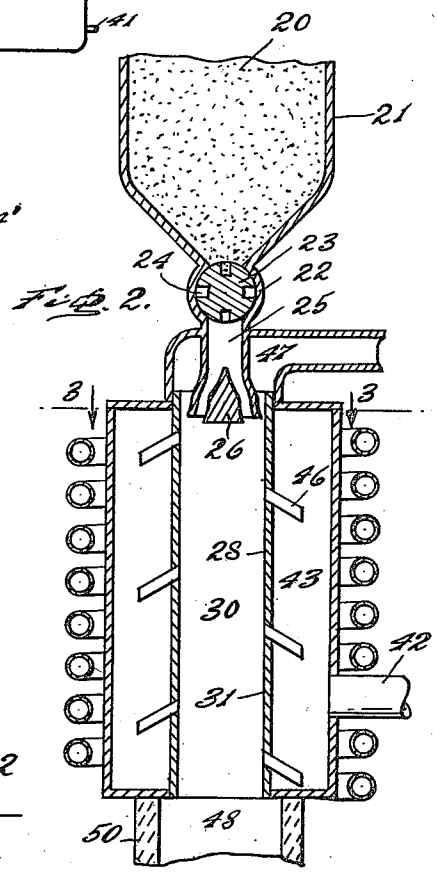
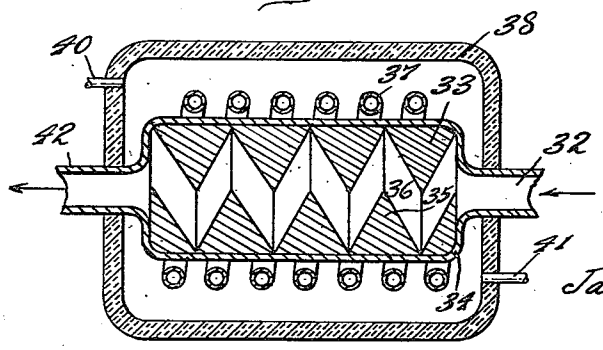


Fig. 4.



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APPARATUS AND PROCESS FOR MELTING MATERIAL OF HIGH MELTING POINT

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Application April 23, 1954, Serial No. 425,273

15 Claims. (Cl. 75—84)

The present invention relates to the melting and desirably also purifying of materials of high melting point, especially metallic zirconium, titanium and hafnium.

A purpose of the invention is to melt individual particles of high melting point material free from contamination by heating the particles by a preheated gas while the particles are free in the gas, desirably supplementing by heat additionally applied in the chamber containing the gas.

A further purpose is to introduce the gas into the chamber in an upward direction or in a swirling direction, or preferably in an upward swirling direction, and thus retard the fall of the particles and desirably also apply centrifugal force to them.

A further purpose is to meter the particles as they are introduced and seal against escape of inert gas, introducing the particles at a rate so low that the particles remain free in the gas.

A further purpose is to employ particles of preferably uniform size and of sufficient size to drop in the gas.

A further purpose is to introduce the particles at the outside of the chamber where they will be most effectively picked up by the swirl.

A further purpose is to preheat the gas in a chamber which preferably consists of the material to be melted so as to minimize the possibility of contamination.

A further purpose is to eliminate impurities as the particles are heated and melted and particularly to carry off magnesium and magnesium chloride from zirconium, titanium and hafnium.

A further purpose is to introduce argon along with helium as the inert gas and thereby facilitate the carrying off of impurities by the gas.

A further purpose is to carry the particles, after they have been heated by the inert gas, through a booster chamber preferably located below the chamber in which the particles are first heated, the booster chamber being maintained at a temperature substantially above the melting point of the material to be melted.

A further purpose is to drop the particles through the booster chamber and desirably also to have the particles swirl in the booster chamber.

A further purpose is to heat the booster chamber by a resistance arc in carbon and desirably to protect the arc against the molten metal and metal vapor by a refractory wall of the booster chamber, preferably also of carbon, and to avoid contamination by dropping the particles through the booster chamber, and thus minimising contact with the chamber wall.

A further purpose is to deposit the molten particles on a continuous casting desirably immediately below the booster chamber and preferably to cool the continuous casting in an atmosphere of inert gas.

A further purpose is to introduce alloy into the particles immediately before they solidify in the continuous casting.

Further purposes appear in the specification and in the claims.

In the drawings I have chosen to illustrate one only of

the numerous embodiments in which my invention may appear, selecting the form shown from the standpoints of convenience in illustration, satisfactory operation and clear demonstration of the principles involved.

Figure 1 is a diagrammatic central vertical section of mechanism in accordance with the invention.

Figure 2 is a fragmentary enlargement of the upper portion of Figure 1.

Figure 3 is a section on the line 3—3 of Figure 2.

Figure 4 is an axial section through one form of gas preheater in accordance with the invention.

Describing in illustration but not in limitation and referring to the drawing:

The present invention is concerned with the melting and purifying of materials of high melting point, especially zirconium and also primarily titanium and hafnium. The principles of the invention in its broader form are also applicable to the melting and purifying of other refractory metals, for example, tungsten, iridium and the noble metals such as platinum, and also to the melting and purifying of highly refractory materials, such as refractory carbides, like the carbides of tungsten, boron and titanium, and refractory oxides such as zirconia, chromium oxide, magnesia and alumina.

Metallic zirconium is commonly obtained by the Krole process, which produces a sponge containing impurities, especially magnesium chloride, and secondarily iron, other metallic oxides and nitrogen. The usual technique for initial purifying is to vacuum distill. Various grades of partially purified zirconium are obtained by vacuum distillation, depending upon the position of the material in the condenser, and these are blended to obtain the purity desired, the most impure material being sent back for reprocessing.

Great difficulty has been encountered in melting zirconium to obtain ingots of high purity.

Because of its high melting point, about 3555° F., zirconium cannot be melted in most refractories, and the use of carbon refractory is prohibited by the fact that carbon is one of the most objectionable impurities in zirconium. Other impurities which are quite objectionable for their effect on rolling are magnesium, magnesium chloride, and nitrogen.

By the present invention it is possible to obtain a very high purity of molten zirconium or other molten material, eliminating impurities such as magnesium and magnesium chloride and avoiding substantial pickup of impurities such as carbon and nitrogen.

In accordance with the present invention, the material to be melted and purified, for example, zirconium sponge, is introduced in the form of particles, preferably of uniform size, and suitably of the order of 1/16 to 1/4 inch in size, although larger or smaller particles can be used as long as the particles are small enough to be retarded by the gas and large enough to prevent them from becoming completely air-borne and from being carried out of the furnace with the gas. If the particles consist of zirconium and are badly contaminated with magnesium chloride, it is possible to remove a large percentage of the magnesium chloride by leaching.

The particles 20 are charged into a hopper 21 at the top of the furnace and the discharge of the particles from the hopper is metered, while at the same time a gas lock is provided, suitably by cylindrical housing 22 at the bottom of the hopper which contains a cylindrical rotor 23 having metering pockets 24 in its periphery. The pockets are large enough to receive a predetermined charge of particles to be melted as the rotor turns, for example at a controlled speed under the action of a suitable drive.

The metering is regulated so that the particles will not clog the furnace but will behave as individually free particles as they pass through the furnace and will in the main

remain separate in the gas. It should be noted that the furnace chamber is not charged full of particles. Any other suitable metering means and gas lock may be used.

The particles drop from the metering device into a charge opening **25** at the bottom of the hopper and are preferably diverted to the outside by a bell **26** supported by a spider **27**.

The particles drop into an initial heating and purifying furnace **28** having an interior suitably vertical preferably cylindrical chamber **30** formed by a vertical tube **31** of a suitable refractory, preferably zirconia in the case of melting zirconium.

Inert gas which in the case of zirconium, titanium, hafnium, tungsten or iridium, will be argon, xenon, neon, krypton or helium or a mixture of the same, is introduced suitably from compressed cylinders or other containers through pipe **32** of preheater **33** consisting of a housing **34** and internal helical walls **35** forming a helical internal passage **36**. The housing **34** and the helical walls **35** are desirably made of the material to be melted, or its oxide, so that where the metal to be melted is zirconium the gas as it is heated will come in contact only with zirconium or zirconia at this stage. The housing and the helical walls are heated by an electric inductor **37** suitably carrying intermediate or high frequency alternating electric current and desirably water cooled. The housing and the inductor is surrounded by heat insulation **38**. The space surrounding the housing is desirably filled with inert gas by an inlet connection **40** and an outlet connection **41**.

Any other suitable means of heating the inert gas may be used. The inert gas is preferably heated in the preheater to a temperature slightly below the melting point of the material being melted. The preheated inert gas passes through pipe **42**, preferably also composed of the same metal which is being melted, into a plenum chamber **43** which is formed around the refractory tube **31**. The plenum chamber on the outside has a refractory wall **44**, which may be formed, depending upon the metal being melted, of carbon or a carbide such as zirconium, titanium or hafnium carbide when zirconium is being melted, or a refractory oxide such as zirconia, and is an electric conductor at the operating temperature, and this is surrounded by inductor coil **45** of an electric induction furnace, suitably at intermediate or high frequency of alternating current, which develops additional heat in the plenum chamber to adjust the temperature of the inert gas to a temperature substantially that of the melting point of the material to be melted, or slightly above the same. It will be understood that the carbon refractory **44** is surrounded by an outer jacket, not shown, containing inert gas to protect against oxidation.

From the plenum chamber the inert gas is projected through jet openings **46** into the furnace chamber **30**. The jet openings will be preferably considerably more numerous than those shown, extending diagonally upwardly and preferably also tangentially to produce a whirl of inert gas at very high temperature in the chamber **30**. This whirl is moving upward. The pressure of the inert gas will suitably be of the order of 10 to 30 p. s. i. gage at room temperature, but of course at the elevated temperature the gas is at much higher pressure in the plenum chamber and in the furnace chamber **30**.

The particles of material to be melted drop into the chamber **30**, preferably near the outside and their fall is retarded by the upward flow of the gas and also by the whirling action. This whirling action causes centrifugal force which is very important in eliminating impurities as the particles melt. It is possible actually to see impurities separate at this stage. In the case of zirconium, impurities such as magnesium and magnesium chloride pass out with the inert gas through flue **47** at the top. The inert gas and impurities are preferably carried to a condenser not shown which separates the impurities, and the inert gas is preferably collected, repurified and reused.

The preferred composition of the inert gas is a mixture of helium with about 25 percent by volume of argon. It has been found that argon is helpful in aiding the separation of impurities from metal such as zirconium, titanium, and hafnium, and it is believed that argon in the content of 5 to 50 percent by volume of the total gas with the balance helium or some other monatomic inert gas is desirable. Nitrogen should at all costs be avoided with zirconium, titanium or hafnium. When melting zirconium, the gas entering the plenum chamber is preferably at a temperature of about 3000° F. and is heated in the plenum chamber to a temperature of about 4000° F. The particular temperature of course will vary with different materials being melted, gas pressure and grain size of the particles.

Magnesium chloride begins to evolve from zirconium at a temperature of about 1300 to 2600° F. The time taken by the particle to fall through the chamber **30** is preferably about 5 to 10 seconds, due to the retardation from the upward flow of the gas and due to the centrifugal force which makes it take a long path. The surface agitation, the centrifugal force and the time of exposure at high temperature are all important factors in eliminating impurities such as magnesium, magnesium chloride, nitrogen and iron from zirconium or the like.

While it will be evident that a succession of whirling gas chambers of the character of the chamber **30** can be used, it is preferred to accomplish the melting by the use of a booster chamber which adds additional heat to the already melted or nearly melted particles which leave the bottom of the chamber **30**. The booster chamber is desirably a zone of very high temperature indeed, through which the particles may drop relatively rapidly. It is ordinarily placed immediately below the chamber **30**. As best seen in Figure 1, a booster chamber **48** suitably of cylindrical form is placed beneath the chamber **30**, and has a suitably vertical tubular refractory wall **50**. The refractory wall **50** is desirably of carbon in the case of melting zirconium, although in suitable cases other refractories may be used such as high melting point carbides like the carbides of zirconium, titanium and hafnium. The temperature prevailing in the chamber **48** is preferably in the range of 6000 to 8000° F. (the larger the particle size, the higher the temperature) when melting zirconium or similar materials, and this temperature may be obtained in any suitable way, but preferably from a carbon resistance arc as disclosed in detail in my application Serial No. 289,373, filed October 30, 1953, for Electric Arc Resistance Furnace. In a carbon resistance arc furnace it is very important to maintain the stability of the arc by protecting it from metal vapor and molten metal of the particles dropping through the chamber **48**, and therefore the refractory wall **50** forms a closed envelope inside the booster furnace **51**.

The booster furnace **51** preferably comprises an inner series of interfitting carbon arcing rings **52** engaged at the top by a carbon resistor contact ring **53** connected to a metallic terminal **54** and engaged at the bottom by a carbon resistor contact ring **55** engaged by metallic terminal **56**. The inner set of arcing rings **52** is preferably surrounded by a relatively spaced outer set of interlocking carbon arcing rings **57** connecting at the top by a carbon resistance contact ring **58** engaged by a metallic terminal **60** and connecting at the bottom with a carbon resistor contact ring **61** engaged by metallic terminal **62**. Insulating spacers are provided at **63** and **64** to separate the inner and outer sets of carbon resistance arcing elements. The entire resistance arc furnace is surrounded by an envelope of inert gas in a container not shown.

As the particles of material to be melted drop through the booster chamber **48** they are still whirling from the action of the gas and of course the chamber **48** is filled with inert gas. The particles complete their melting if they are not already melted and preferably become very highly superheated in the booster chamber **48** so that they are extremely fluid indeed by the time they reach the

bottom of this chamber. The last vaporizable impurities pass off under very high superheat aided by the whirling action in the booster furnace.

An important aspect of this invention is that the particles drop quickly through the chamber **48** without any intimate or prolonged contact with the carbon refractory wall, since the chamber wall has no projections into the path of the particles, being of uniform cross section. Thus it is possible to secure a very low carbon content in the resulting ingot notwithstanding the carbon refractory wall at this point. This is very important with zirconium where a substantial carbon content may make the metal unrollable.

It will be understood that where desired an electric induction furnace may be substituted instead of the Ballantine carbon resistance arc.

When it is desired to make an ingot, the molten particles are deposited at **65** in a continuous casting mechanism **66** at the top of a continuously forming ingot **67** which is withdrawn by motor **68** and worm **70** engaging worm wheel **71** which forms a nut on screw **72** connected to the ingot, the nut being held by a bearing not shown. The solidifying collar **73** of the continuous casting apparatus, suitably of copper or the like, surrounds the ingot at the point of solidification, and is water-cooled, introducing water at **74** and withdrawing it at **74'**. The solidifying collar has a reverse taper **75** (in the direction of withdrawal) to aid in withdrawing the ingot.

In order to protect the ingot against oxidation, it is surrounded by a jacket **76** below the cooler having inert gas at **77** provided with a gas tight seal at **78** against the ingot. The inert gas is brought in by pipe **77'** and withdrawn by pipe **77²**.

The very high superheat is important in obtaining a homogeneous solid ingot free from blow holes. There is so much superheat in each globule as it comes down that it melts the adjoining metal below it and forms a firm and continuous metallic bond as it solidifies.

In some cases it is desired to insert alloying ingredients, and provision is made for this by a tube **80** extending into the chamber **48** immediately above the point of solidification and directing a stream of alloying ingredients on the top of the ingot. It has been found that even relatively volatile alloying ingredients can be introduced at this point, and although alloy loss is suffered, it is not prohibitive. For example such materials as tin have been alloyed with zirconium by this method, the tin particles being introduced among the depositing globules as they are still molten and beginning to solidify.

By way of example, in experiments conducted using the process and furnace of the invention, the chamber **30** has been slightly smaller than 3" in inside diameter and from 24" to 36" long and chamber **48** has been about 3" in inside diameter and approximately 6" long.

The gas has been fed to the chamber **30** at the rate of approximately 150 cubic feet per hour, measured at standard conditions of temperature and pressure.

In melting heavy metals (having specific gravity greater than 12) the rate of feed to the furnace has been about 20 pounds per hour. With metals having specific gravity below 12, the rate of feed has been considerably higher of the order of 75 pounds per hour.

It will be evident that one of the very important aspects of the invention is the heating and melting of the particles as they are floating in or slowly dropping through the inert gas.

It will further be evident that another important aspect is the whirling action which greatly assists both in heating and also in centrifugal elimination of impurities.

It will further be evident that an important aspect of the invention is dropping of the particles past a wall of carbon refractory without holding the particles in intimate contact with the wall so that contamination will be minimized.

It will further be evident that an important aspect of the invention is the depositing of very highly superheated globules of molten metal on the continuous casting so that each globule will melt adjoining metal below it and assure uniformity.

In view of my invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the process and apparatus shown, and I, therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. The process of melting a high melting material free from contamination, which comprises preheating inert gas in a separate preheating chamber, metering particles of the material to be melted at a rate sufficiently low so that the particles will pass through a first furnace chamber individually, introducing the metered particles of the material to be melted near the top of the first furnace chamber, passing the inert gas from the preheating chamber into the first furnace chamber and separating the particles by the gas in the furnace chamber and thereby retarding the downward flow of the particles while heating the individual particles of the material to be melted by the sensible heat of the inert gas, additionally heating the first furnace chamber, dropping the particles through the first furnace chamber into a second booster furnace chamber below the first, and also containing the inert gas, and in the booster chamber heating the particles to a temperature substantially above the melting point of the material to be melted.

2. The process according to claim 1, which comprises introducing the inert gas into the first furnace chamber in a swirl direction and carrying the particles with the inert gas in centrifugal motion.

3. The process according to claim 1, which comprises introducing the inert gas into the first furnace chamber in an upward direction and dropping the particles through the inert gas while retarding the fall of the particles by the inert gas.

4. The process according to claim 1, in which the particles are of substantially uniform size.

5. The process according to claim 1, which comprises preheating the inert gas in the preheating chamber while in contact with material of the same character as the material to be melted.

6. The process according to claim 1, in which the material to be melted is a metal of a class consisting of zirconium, titanium, hafnium, iridium and tungsten.

7. The process according to claim 1, which comprises swirling the particles as they drop through the booster chamber.

8. The process according to claim 1, in which the booster chamber is composed of carbon, which comprises dropping the particles through the booster chamber and thereby avoiding contamination with the carbon.

9. The process according to claim 1, which comprises heating the booster chamber by resistance arc in carbon, protecting the arc against the molten metal and metal vapor and dropping the particles through the booster chamber and thereby avoiding contamination with the booster chamber wall.

10. A furnace for melting materials of high melting point, comprising a preheater for preheating a stream of inert gas, a first vertical furnace chamber, means for metering particles to be melted and introducing the particles at the top of the first furnace chamber at a rate so low that the particles pass through the first furnace chamber individually, means for introducing the preheated inert gas into said first furnace chamber and thereby heating the individual particles of material to be melted while they are free in the inert gas, means for additionally heating the first furnace chamber, a second booster furnace chamber vertically below the first furnace

chamber and means for heating the booster furnace chamber to a temperature substantially above the melting point of the material to be melted.

11. A furnace according to claim 10, in which the means for introducing the preheated gas into the first furnace chamber comprises upwardly directed jets.

12. A furnace according to claim 10, in which the means for introducing the inert gas into the first furnace chamber comprises circumferentially and upwardly directed jets.

13. A furnace according to claim 10, in which the wall of the preheater for the inert gas is composed of the same material as the material being melted.

14. A furnace according to claim 10, in which the means for heating the booster chamber consists of a resistance arc in carbon.

15. A furnace according to claim 10, in which the booster chamber has a carbon refractory inner wall and the means for heating the booster chamber consists of a resistance arc in carbon surrounding the carbon refractory wall.

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