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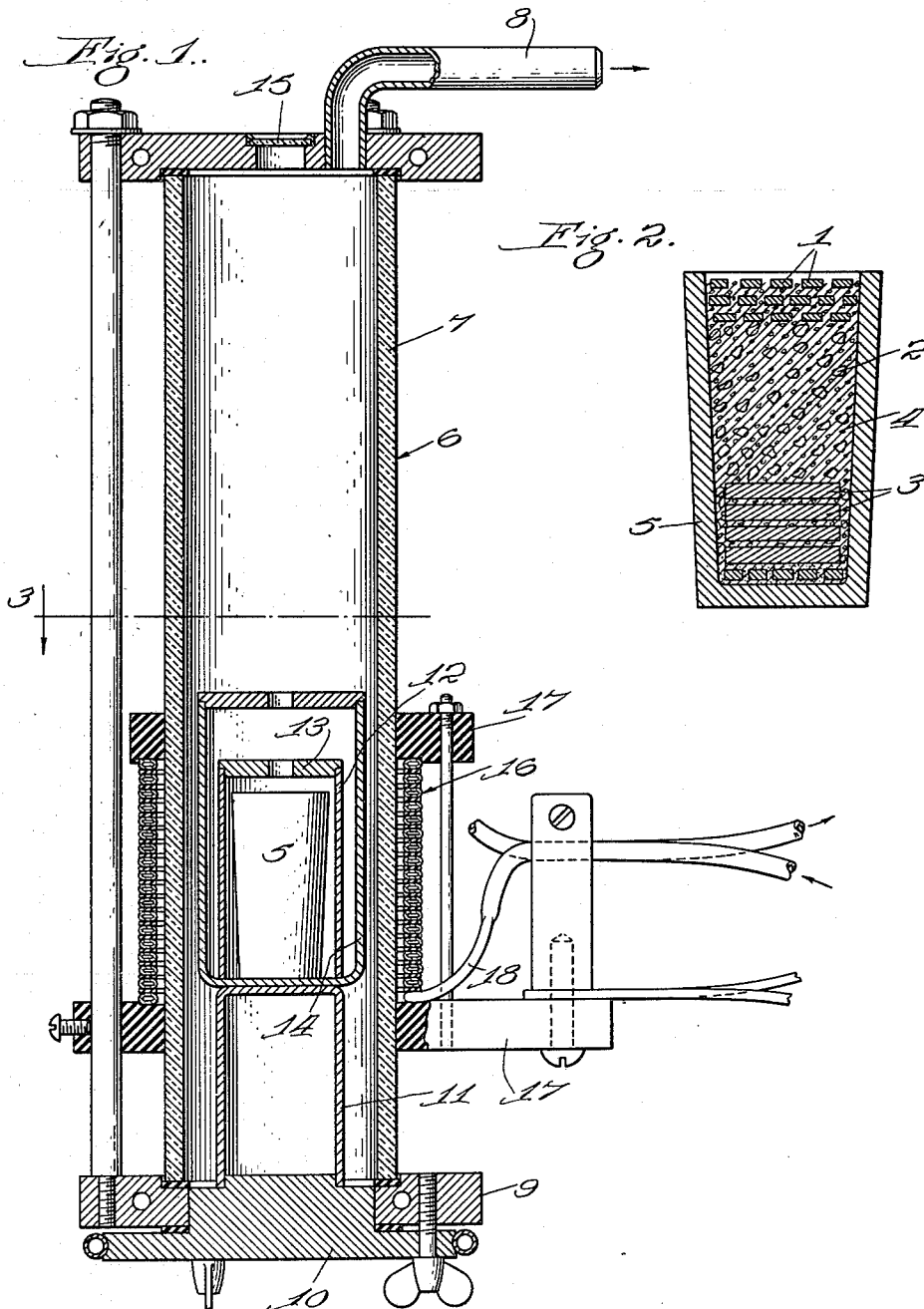
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2,048,706

METHOD OF MAKING ALLOYS

Filed Nov. 15, 1934

6 Sheets-Sheet 1



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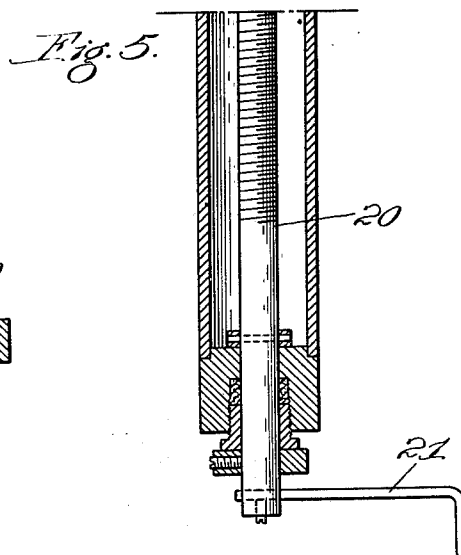
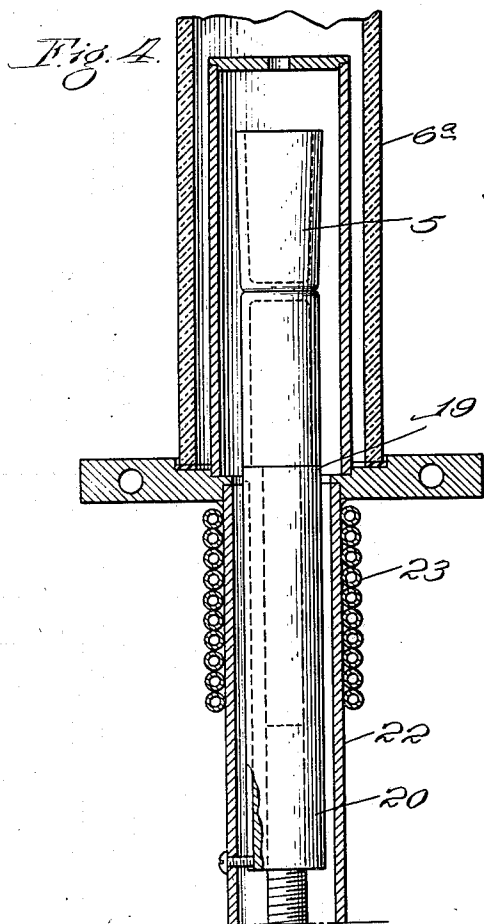
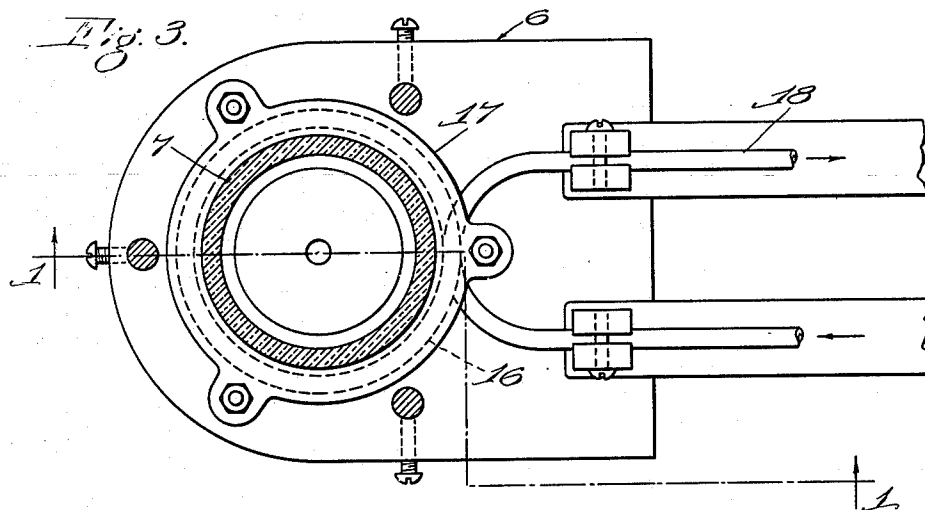
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METHOD OF MAKING ALLOYS

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6 Sheets-Sheet 2



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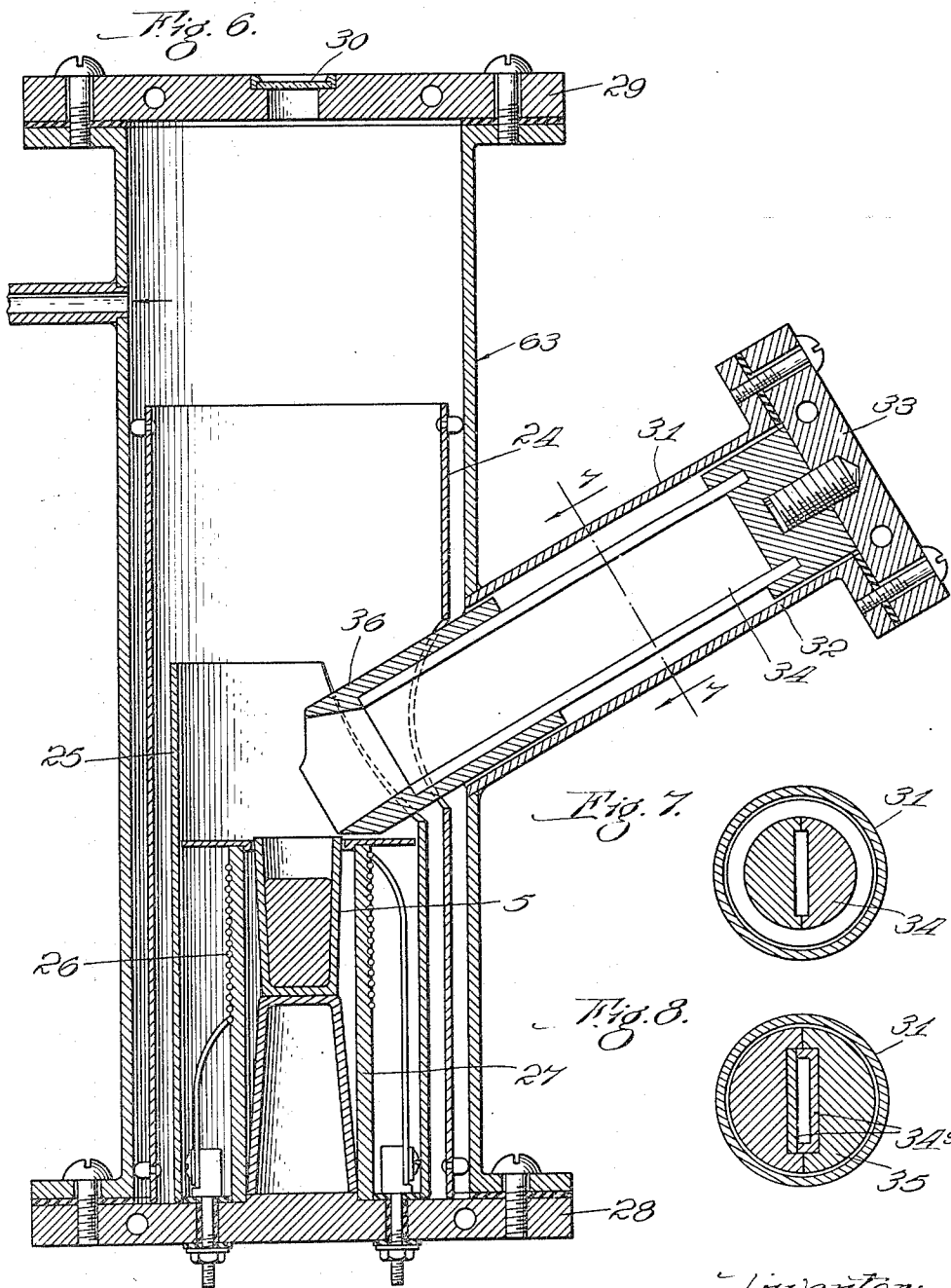
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METHOD OF MAKING ALLOYS

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6 Sheets-Sheet 3



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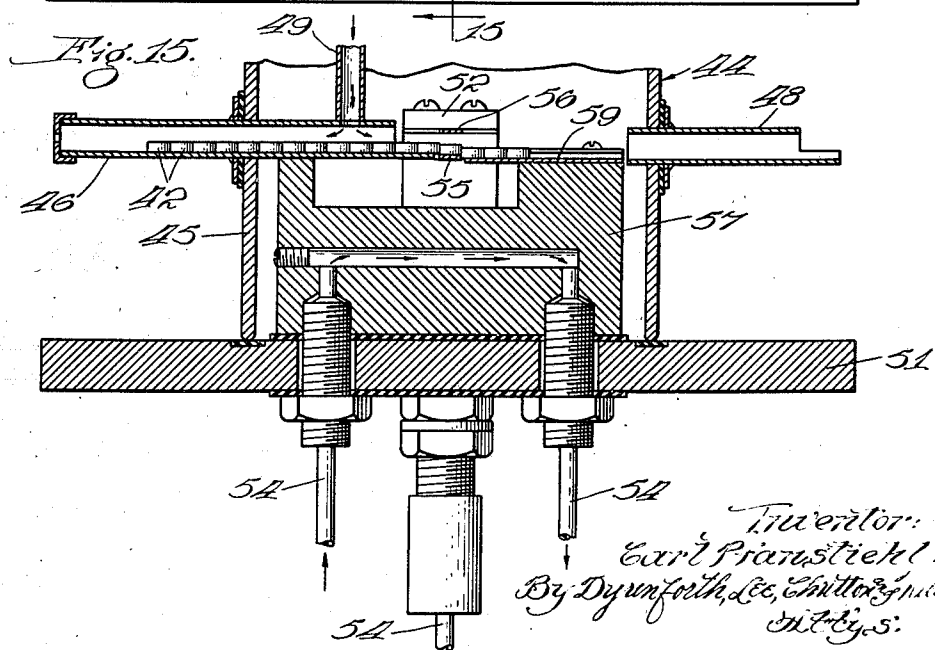
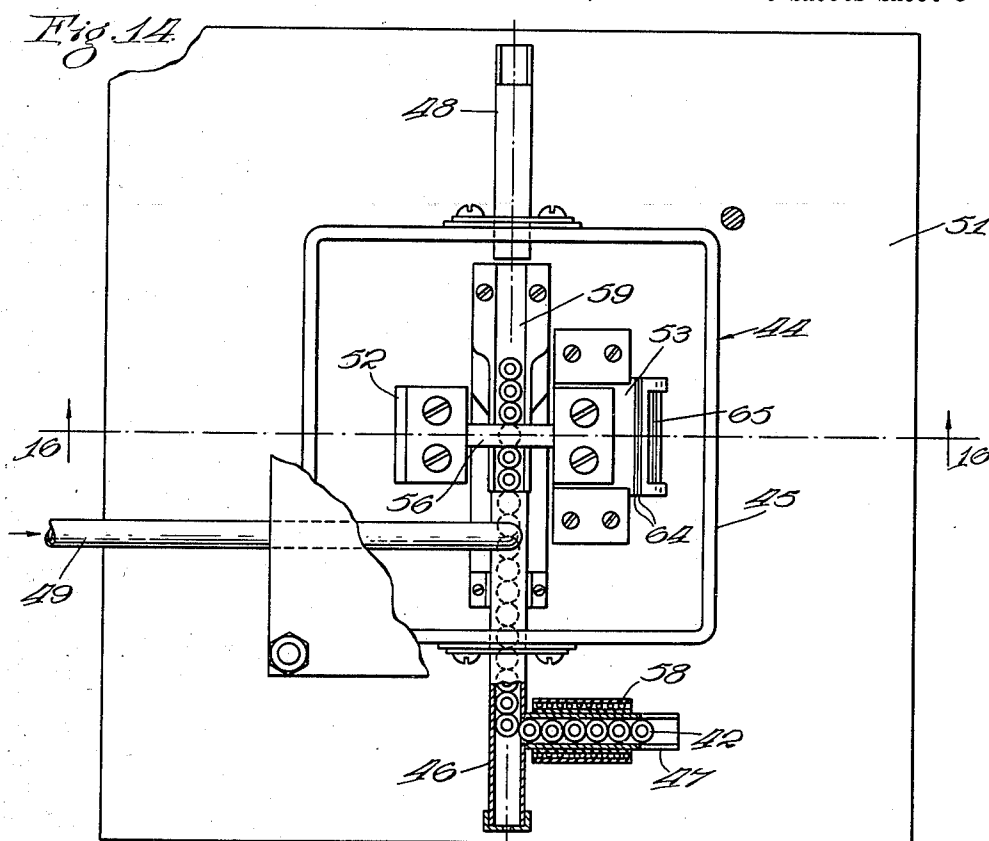
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METHOD OF MAKING ALLOYS

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6 Sheets-Sheet 6

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UNITED STATES PATENT OFFICE

2,048,706

METHOD OF MAKING ALLOYS

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Application November 15, 1934, Serial No. 753,219

14 Claims. (Cl. 75—135)

This invention relates to a method of producing tough alloys from alloys customarily fragile or brittle.

In my co-pending application Serial No. 753,220 filed November 15, 1934, is described an alloy having the preferred composition of 35 to 50 parts cobalt, 30 to 40 parts chromium, 15 to 25 parts tungsten and 3 to 5 parts of carbon. The percentage of tungsten carbides, chromium carbides and complex double carbides in this alloy is so great that when produced in the ordinary manner the material has a mass of large crystals which render it brittle. It has now been discovered, however, that this alloy may be produced in a tough form by rapidly cooling it to produce finely divided crystals. It has also been discovered that by heating an alloy rich in carbides to a temperature several hundred degrees above the melting point more of the carbides can be dissolved in the matrix and will be retained therein on sudden cooling, producing a tougher, harder and more chemically resistant matrix.

An apparatus for securing such cooling is illustrated in the drawings in which—

Fig. 1 is a broken elevation, partly in section, of a vacuum furnace for fluxing of the alloy;

Fig. 2, a vertical section through a crucible, showing the method of loading the ingredients of the alloy therein;

Fig. 3 is a section along line 3 in Fig. 1;

Fig. 4 shows a broken sectional elevation of a modified furnace provided with means for lowering the crucible into a water-cooled area for quick cooling of the alloy;

Fig. 5 is a sectional elevation which is an extension of the lower portion of Fig. 4;

Fig. 6 is a broken sectional elevation of a furnace which is provided with a chilled mold into which the alloy may be poured for shock cooling;

Fig. 7 is a section along the line 7 in Fig. 6;

Fig. 8 is a similar section with a modified mold;

Fig. 9 is a broken sectional elevation showing the furnace in Fig. 6 tilted to pour the alloy into the mold;

Fig. 10 is a perspective view of a slug of alloy from the mold;

Fig. 11 is an elevation partly in section illustrating a magnet for weighing of the alloy into measured charges;

Fig. 12 is an elevation similar to Fig. 11 showing the discharge of the alloy into a smaller mold;

Fig. 13 is a sectional elevation of a lime button or mold for the production of small globules of the alloy;

Fig. 14 is a plan view, partly in section and

partly broken away, of a furnace for the rapid fusion and rapid cooling of globules of the alloy in the lime molds;

Fig. 15 is a section elevation along the line 15 in Fig. 14;

Fig. 16 is a section view taken along the line 16—16 in Fig. 14;

Fig. 17 is an end of the slide terminal block; and

Fig. 18 is a diagrammatic sketch of an apparatus for welding the globules to a tip.

The invention will be described primarily in connection with the production of tough alloys of a cobalt type matrix, and rich in chromium or tungsten carbides. Alloys of this type, when produced in the form of fine crystals, are extremely hard, tough and inert. Nevertheless many of them are extremely sensitive to oxidation at temperatures near and above the melting point and it is therefore important that the fusion steps of the process be carried out in the absence of oxygen.

It is likewise of importance in many instances that the metals themselves be in a very pure form. For the preferred high carbon alloy, the tungsten used is preferably pure wrought tungsten, and is preferably used in dense form rather than in powder. The carbon is preferably pure carbon, such as Aitcheson graphite electrodes. The chromium is preferably pure electrolytic chromium deposited in small flakes and nodules having a thickness of .01 to .03 inch, and an average diameter of $\frac{1}{16}$ to $\frac{1}{8}$ inch.

The ingredients, in the desired proportions, may be mixed in a crucible, for example as illustrated in Fig. 2, in which 1 represents tungsten discs; 2, chromium flakes; 3, cobalt discs and the small particles 4 are the carbon, all of them contained in the crucible 5.

Considerable difficulty is encountered in the selection of a proper crucible, but it has been found that a good grade of magnesium oxide crucible is satisfactory.

In preparing the original melt of alloy the crucible 5 is filled as described, and is placed in a furnace 6, as shown in Fig. 1. This furnace, which is adapted to be evacuated, or to be supplied with an inert gas, comprises a quartz cylinder 7 provided with a connection 8 leading to a vacuum pump. The cylinder is set in a base 9 which is provided with a plate 10 cooled preferably by water-cooling. The crucible 5 sits in the furnace upon a support 11 and is provided with a graphite sleeve 12 which has a graphite cap 13. This is likewise surrounded by a protecting cru-

cible 14. A pyrex glass window 15 is provided at the top of the furnace, and the various caps are provided with peep holes so that observations may be made upon the alloy.

It is preferred to operate in a vacuum to avoid contamination and porosity of the alloy, and after a proper vacuum has been reached in the furnace, preferably as low as .1 mm., the ingredients are fused by means of a high frequency inductor coil 16 which is wrapped about the cylinder 7 at the height of the crucible. This coil is set in hard asbestos supports 17 and is in the form of a flattened copper tube 18, through which cooling water circulates. The use of a high frequency inductor coil causes violent stirring of the alloy, and is therefore much preferred for this initial fluxing.

After the alloy has been melted and held at a temperature several hundred degrees above its melting point for a period long enough to free it from volatile matter, during which time the gases also remove other contaminating matter, the current may be cut off and the alloy cooled. Such a heating period is normally about 20 minutes. When cooled in the furnace, however, even though the base and roof of the furnace are water-cooled, the cooling is so slow that the crystals of the alloy are relatively very large, and a relatively brittle metal is produced. The crystals are large enough so that on grinding or powdering of the alloy, it is not certain that uniform mixes will be obtained, and it is therefore preferred to remelt the alloy and cool it in a small slug in order to produce smaller crystals.

Fig. 4 represents an optional furnace 6^a provided with a movable bottom 19 mounted on screw shaft 20 and adapted to be lowered by turning of the crank 21. In this manner the crucible 5 may be lowered with the molten alloy within the steel cylinder 22 and directly within the area of the water-cooling coil 23. With this apparatus it is possible to procure much more rapid cooling of the alloy, and to produce crystals of such a size that on grinding they will give a substantially uniform mixture.

It is preferred, however, with the present apparatus, to remelt the high carbide alloys and freeze them in the form of thinner slugs of metal. It is appreciated that by proper mechanical development, the furnace 6 may be provided with means whereby the alloy could be poured directly into a mold. This may be done with the present furnace but it is preferred to use a second heating treatment in a vacuum furnace 63 of the type shown in Fig. 6. This furnace in general corresponds to that shown in Fig. 1, but it is provided with a metal shield 24 about a graphite shield 25 and is heated by an electric-resistance element 26 within the furnace. Preferably the resistance element is of tungsten or molybdenum, and is wound about an "Alundum" tube 27 in which the crucible 5 is set. The base 28 and top 29 of the furnace are preferably water-cooled, and the top is provided with a pyrex window 30. Immediately above and to one side of the crucible and inclined with respect thereto is the mold container 31 which comprises a seamless steel tube 32 having a water-cooled end plate 33 into which is screwed a graphite mold 34. As shown in Fig. 7 the mold is shaped to provide a central opening of small cross section. Normally the slug of alloy should be not more than $\frac{1}{8}$ inch in thickness, and the preferred dimensions are $\frac{3}{4}$ x 1 x 3 inches. In Fig. 8 is shown a copper mold 35 lined with graphite 34^a.

A graphite funnel 36 is provided at the mouth of the mold. In preparing the ingot or slug, the crucible with its contents is placed inside of the furnace 63 and, after a vacuum has been drawn, is fused by the heat of the electric-resistance element 26. The vacuum is preferably as low as .05 to .1 mm. The fusion is continued for some time, and preferably the temperature of the molten metal is carried to a point sufficient to produce a uniform solution, for example, a temperature high enough to dissolve all of the carbides. This may be from 200 to 500 degrees above the melting point. The temperature is maintained long enough to reach equilibrium. The melting point of the ordinary alloy of this type is about 2375° F., and the temperature is preferably carried to about 2850° F. for the specific chromium, tungsten, cobalt, high carbon alloys. After the temperature has reached the desired point, the furnace is lifted, and tilted to pour the alloy into the mold 34, as shown in Fig. 9. This mold in effect constitutes a water-cooled chill, lined with graphite. The alloy solidifies in about 2 or 3 seconds in this mold, to form a slug or ingot 37 as shown in Fig. 10. When cooled in this manner the crystals of the alloy are finer than in the original slug.

After cooling, the ingot is removed and broken up into fine particles. This may be readily accomplished by grinding in a steel mortar with a steel pestle. The material is broken into small particles. The particles are then sifted, and it is preferred to use those that pass a 30 mesh screen and remain on a 100 mesh screen.

After crushing and screening to pass a 30 mesh and to be caught upon a 100 mesh screen, a small amount of the powdered alloy is put into a mold for re-fusing. It has been found that the powder is slightly magnetic, and an accurate and speedy way of measuring the same into the molds may be had by the use of a magnet. A form of magnet 38 is shown in Fig. 11, and comprises a fine soft iron wire 39 somewhat smaller than a pencil lead inserted in a bakelite cylinder 40 and surrounded by copper wire winding 41. By dipping this magnet into the powder, a measured charge may be picked up, and the amount of the charge may be varied by adjustment of the current through the coil 41.

The charge is then carried and dropped into a mold 42 preparatory to further fusion. The mold preferably consists of a lime button having a central depression 43, as shown in Fig. 13. This lime is preferably a specially treated lime which has been heated for a considerable period after the removal of all carbon dioxide at a temperature considerably above the normal calcining temperature. The lime thus produced has unusual properties of stability in air as well as producing a stronger mold. In loading the powdered alloy into the lime molds, it is preferred to dust it lightly with powder of the same lime. This prevents sticking to the mold, which otherwise may occur in some instances.

After loading the charge into the boat or mold, the latter is placed in the electric furnace 44. This furnace comprises an air-tight jacket 45 provided with an inlet 49 for the introduction of pure hydrogen gas, and also provided with seamless steel tubes 46, 47 and 48 about $\frac{1}{4}$ inch square for the introduction and ejection of molds. The furnace is provided at the top and at the bottom with water-cooled plates 50 and 51, respectively. The side walls 45 of the jacket are preferably of seamless steel tubing.

Copper terminals 52 and 53 are provided in the furnace, the bottom plate 51 being drilled to permit the necessary connections, and to permit water-cooling of the terminals. Cooling pipes are indicated at 54. Two tungsten strips 55 and 56, one about $\frac{1}{8}$ inch above the other, connect the two terminals. These strips are normally about .025 inch in thickness, by $\frac{1}{4}$ of an inch wide, by $2\frac{1}{2}$ inches long. Directly above the lower strip 55 is provided a water-cooled copper block 57. The furnace is as a whole constructed so that when removed from the tungsten filament 55 the molds will be subjected to as much cooling action as possible, to the end that the alloy will be cooled in the shortest possible length of time.

The terminal 53 is slidably mounted on the block 630 in order to provide for expansion of the heating elements. The spring 65 tends to move the terminal with the expansion of the tungsten strips and holds the strips straight. The flexible copper strips 64 provide the electric connection to the terminal.

Before putting the furnace into operation a stream of hydrogen gas is admitted through the tube 49 and the furnace completely cleared of all oxygen. The hydrogen used should be of extreme purity, and it is advisable to treat even the best hydrogen on the market to remove all traces of water and oxygen therefrom. The hydrogen leaves the furnace through the openings 46, 47 and 48, through which a gentle current of the gas is maintained.

The loaded lime boats or buttons are preferably inserted in the arm 47 which is heated by a resistance coil 58 about the tube. It is preferred to raise the temperature to about 200° C. to expel all oxygen from the molds. They are then pushed through the arm 47 into the tube 46, and then by a small wire (not shown) operating through a small hole in the end of the tube 46 on to the tungsten filament 55. The tube 46 extends almost to the filament 55, and the hydrogen inlet 49 preferably enters this tube a short distance from its inner end. In this manner a current of hydrogen is maintained across the filament in the direction of passage of the molds, through the furnace, so that any material volatilized on the filament will not settle on or condense on the incoming alloy. In passing to and from the filament the molds pass along the water-cooled copper slide 59 set upon the water-cooled copper block 57. The alloy is thus kept well below fusion up to the time that it is pushed on to the filament and is immediately frozen upon leaving the same.

The filaments are heated continuously and the buttons are left on the lower one for about 5 to 15 seconds. As soon as the powdered alloy melts, it spheroid itself by surface tension, and maintains this spheroidal shape thereafter. The heating is continued for about 5 to 15 seconds, during which time the temperature may be carried several hundred degrees above the melting point of the alloy, in order to produce a uniform alloy.

In heating the furnace a preferred current is 850 amperes with one volt. With this current a hot spot about $\frac{1}{2}$ inch long is produced in the center of the filaments, in the center of which the mold sits.

After the alloy is thoroughly fused, the lime button is pushed off the tungsten filament on to the copper runway 59 where it is almost instantly frozen. The size of the spheroid is such that the freezing will occur in an extremely short time,

and preferably should take place in about one second or less. It is therefore preferred that the diameter of the spheroid be of the order of $\frac{1}{16}$ th of an inch or less in the case of high carbide alloys. When produced in this manner the alloy is tough, extremely hard and resistant, and is particularly valuable for use in pen-points.

The structure may be further altered by attaching the spheroid to a metal base, for instance as described in my Patent 2,005,752, issued June 25, 1935, and then fusing and welding the spheroid to the base in an inert atmosphere. Cooling is somewhat more rapid under this condition, and there is a tendency to produce finer crystals.

The final welding operation in some instances of high carbide alloys is preferably conducted so that the spheroid remains fused for 2 to 3 seconds. In some instances this produces a finer crystal structure than where it is instantly fused and then instantly solidified. This is preferred for an alloy composed of 46.7% cobalt, 30.8% chromium, 19.2% tungsten, and 3.3% carbon.

The diagrammatic welding step is illustrated in Fig. 18 showing a tipped base 60 to which a spheroid 61 has been tacked. The spheroid may then be welded to the base by operation of the arc 62 in an inert atmosphere.

Apparently owing to the large proportion of carbides, the alloy is somewhat resistant to welding to certain metals such as gold. For example, in welding as described in my co-pending application Serial No. 706,565 the alloy to gold pen-points, for use as a pen-tip, some 10% of the welds may fail. It has been discovered that this difficulty may be overcome by coating the spheroid with gold, or with a metal readily weldable to the pen-point, and then carrying out the weld.

A preferred method of coating the spheroid is to mix a small proportion of gold with the powder before fusing in the furnace 45. For some reason, not yet fully understood, the gold is expelled from the alloy and substantially all of it coats the exterior of the spheroid. Gold may be added to the finished spheroid in the same manner, and will coat it by surface tension, but the former method is preferred.

A gold plated ball of this type welds readily to a pen-nib. Sufficient gold is applied to produce a coating from .001 to .005 inch thick. The gold may be, for example, from 14 to 24 karat gold, as desired. As an example, 18 karat gold containing 10 to 15% silver and 10 to 15% copper may be employed. A gold coated spheroid should not be maintained at fusion temperature more than a few seconds, inasmuch as if left more than a minute the gold is likely to evaporate. Other metals not alloying easily with the alloy may be used.

The present invention is particularly applicable to a method of spheroiding high melting point metals—that is, with a melting point over say, 2200° F.—for which there is now available no other practicable method. For this purpose, the spheroids produced must be of such a small size that the fused metal will spheroid itself by reason of its surface tension. Normally this size will not greatly exceed $\frac{1}{16}$ th inch in diameter.

The invention is applicable to all metals in which it is desired to produce a finer crystal structure. It is particularly applicable of course to high carbide tungsten, chromium, and cobalt

alloys wherein a normally crystalline material may be substantially unusable.

Moreover, not only are the crystals made finer, but their amount may be decreased. For example, in tungsten, cobalt, chromium carbide alloys, the matrix may be supersaturated with carbides in solid solution, due to the sudden cooling, thus reducing the amount present in segregated crystals.

This supersaturation may be of particular importance where the alloy has to be heated above its melting point to dissolve all the carbides.

Moreover, the supersaturated matrix may be chemically and physically better than the normal matrix.

In some instances it may be possible so to supersaturate the matrix that a uniform homogeneous metal will be produced.

When the alloy is fused in hydrogen, it should not be maintained in fused state for a long period, or gas may be absorbed.

The foregoing detailed description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible in view of the prior art.

What I regard as new and desire to secure by Letters Patent, is:

1. The method of treating an alloy having the approximate composition cobalt 35 to 50 parts, chromium 30 to 40 parts, tungsten 15 to 25 parts, and carbon 3 to 5 parts, which comprises fusing the alloy and freezing it, the freezing being accomplished in a time of the order of 3 seconds, granulating the resulting solid, heating a small portion of the resulting material to a temperature several hundred degrees above fusion, and freezing it in a time of the order of one second.

2. The method as set forth in claim 1, in which the fusion and cooling are carried out in an inert atmosphere.

3. The method as set forth in claim 1, in which the fusion and cooling are carried out in an inert atmosphere, and in which the alloy is primarily produced by mixing the ingredients and then melting them in a high frequency vacuum furnace.

4. The method of producing a tough alloy having the approximate composition cobalt 35 to 50 parts, chromium 30 to 40 parts, tungsten 15 to 25 parts, and carbon 3 to 5 parts, which comprises fusing the alloy and freezing it, the freezing being accomplished in a time of the order of 3 seconds, granulating the resulting solid, heating a small portion of the resulting material to a temperature several hundred degrees above fusion, freezing it in a time of the order of one second, tacking the alloy to a metallic base, the area of contact being small, fus-

ing it by heat supplied substantially entirely through the alloy, and then suddenly freezing it in a time of the order of $\frac{1}{2}$ second.

5. The method as set forth in claim 4, in which the base is a gold base and alloy is lightly coated with gold prior to the welding operation.

6. The method as set forth in claim 4, in which a small amount of gold is mixed with the granulated alloy, whereby on fusion a thin gold coating is produced on the resulting spheroid.

7. The method of producing coated tungsten-chromium-cobalt-carbon alloy spheroids which comprises mixing gold with alloy, and fusing the mixture in a portion small enough to spheroid itself by surface tension, and solidifying the spheroid, whereby the gold is substantially repelled to the surface, and produces a uniform coating thereon.

8. In the production of alloys having the approximate composition cobalt 35 to 50 parts, 20 chromium 30 to 40 parts, tungsten 15 to 25 parts, and carbon 3 to 5 parts, in which a series of open molds containing granulated alloy are placed in line approaching a heating element whereon the alloy is fused, the step of maintaining a current of inert gas across the molds adjacent to the heating element, in the direction of the heating element, whereby the granulated material is kept free from matter volatilized upon the heating element.

9. The method of forming a corrosion resistant alloy of the approximate composition cobalt 35 to 50 parts, chromium 30 to 40 parts, tungsten 15 to 25 parts, and carbon 3 to 5 parts which comprises heating material in quantity to produce a spheroid of such composition of a diameter of the order of $\frac{1}{4}$ inch or less to a temperature at which the material will form a spheroid by surface tension, and freezing the resulting spheroid from such temperature in a time of the order of one second or less.

10. The method as set forth in claim 9 in which the temperature is several hundred degrees above the fusion point.

11. The method as set forth in claim 9 in which the spheroid is re-fused and frozen to a metallic base while depending therefrom.

12. The method as set forth in claim 9 in which the fusion is carried out in an inert atmosphere.

13. The method as set forth in claim 7 in which the alloy has the approximate composition cobalt 35-50 parts, chromium 30 to 40 parts, tungsten 15 to 25 parts, and carbon 3 to 5 parts.

14. The step in making spheroids of cobalt-chromium-tungsten-carbon alloys which comprises melting small quantities of the material for the spheroid on a lime surface.

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