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ALLOY

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My invention relates to alloys and more particularly to a method of forming alloys between a refractory metal and a chemically reactive metal that is volatile at a comparatively low temperature.

An object of my invention is to provide an alloy of a metal or a plurality of metals having comparatively high melting points with one or more metals that are chemically reactive and volatile at a comparatively low temperature.

Another object of my invention is to provide an alloy comprising a highly refractory metal and an alkali or an alkaline earth metal that is adapted to be swaged and drawn into filaments suitable for utilization as cathodes in thermionic discharge devices.

A further object of my invention is to provide an improved method of producing alloys from which the cathodes of space discharge devices may be manufactured that have a comparatively high specific resistance, that may be made from cheap and readily obtainable materials, and that have good physical properties at high temperatures.

A still further object of my invention is to provide improved vacuum tubes or space discharge devices, and especially those of the three or four electrode type, having output and control electrodes and a cathode comprising an alloy that is capable of emitting electrons at elevated temperatures.

It is well known that when filamentary material is coated with an alkaline earth oxide, the electron emissivity of such material is greatly increased. Oxide-coated filaments, however, are not entirely satisfactory as it is difficult to produce filaments of this type which have uniform thermionic properties. Furthermore, such filaments have a rough, soft surface, which becomes easily contaminated and, as a rule, the oxide coating is not sufficiently adherent to prevent its partial removal during the handling of the filament while it is being mounted in the tube.

The mechanism of thermionic emission from oxide-coated surfaces is not clearly understood, but according to the latest theory, part of the oxide is reduced to the metallic state in minute quantities and forms a superficial film of high thermionic activity.

In making experiments in accordance with the above specified theory, I have made the discovery that when an alkali or an alkaline earth metal is alloyed with a metal that is suitable as a base for electron-emitting bodies, such as nickel, a filamentary material is provided that not only gives good electron emission, but is free from the disadvantages resulting from the use of oxide-coated material.

Alloys of a refractory metal, such as nickel, cobalt, iron, titanium, or mixtures of such metals, with metals of the alkali or alkaline earth groups cannot be effectively prepared by the ordinary metallurgical processes because of the high volatility and the extremely great chemical activity of the alkali or alkaline earth metals. Attempts to prepare such alloys by the usual method of heating and mixing have not been satisfactory because the alkali or alkaline earth metals completely volatilize at the high temperature necessary to melt the refractory metal.

I have made the discovery that an alloy comprising one or more highly refractory metals, such as nickel, cobalt, iron or a mixture of one or more of such metals with titanium, or other refractory metals which are added to improve the thermionic properties of cathodes, and one or more of the alkali or alkaline earth metals can be prepared according to a specific process by means of which the former difficulties can be avoided, and an alloy produced that is capable of being swaged and drawn into a filament which gives good electron emission when utilized as the cathode in thermionic discharge devices.

In practicing my invention, a compound of an alkali metal, such as potassium, sodium, lithium, caesium or an alkaline earth metal, such as barium, calcium, strontium or magnesium, or a mixture of two or more of such compounds, is finely ground and mixed with one or more refractory metals, which are also in a fine state of division. Such metals are volatile at temperatures below 900° C., and when a volatile metal is mentioned in

the claims, it will be understood that a metal having a volatilization temperature lower than the temperature stated is intended. The powdered mixture is subjected to pressure in a mold to form coherent briquettes or slugs which are subsequently heated in a vacuum furnace to a temperature above the decomposition point of the compound of the alkali or alkaline earth metal which was employed. The gaseous products of the decomposition as well as any adsorbed moisture are removed by means of vacuum pumps while the mixture is being heated. The temperature of the resulting powdered mixture comprising the refractory metal and the metal of the alkali or alkaline earth is then increased to a red heat to cause the alkali metal or alkaline earth metal to diffuse into the refractory metal.

The briquette or slug, thus formed, is worked into a wire by any suitable means such as by alternately swaging and heating, care being exercised to avoid the action of deleterious gases upon the alloy while it is hot until the original porosity of the briquette or slug has been eliminated by mechanical reduction.

The following specific example will serve to illustrate and explain my invention, although I do not desire to limit my invention to the exact metals or compounds specified as it will be understood that my invention relates broadly to alloys comprising one or more refractory metals, that is, metals which have a melting point above 900° C., and one or more of the alkali or alkaline earth metals, and to the process of producing same.

Finely divided nickel oxide was first reduced to metallic nickel by the action of hydrogen. From 75 to 95% by weight of the powdered nickel, thus obtained, was then mixed with from 25% to 5% by weight of finely ground barium trinitride, $Ba(N_3)_2$, and the mixture subjected to sufficient pressure in a mold to form coherent briquettes. The briquettes were next heated to approximately 150° C. in a high vacuum furnace provided with a vacuum pump to remove moisture and adsorbed gases and were then progressively subjected to a slowly increasing temperature, such as by gradually moving them into a hotter zone of the furnace, a high vacuum being constantly maintained. At approximately 200° C., the barium trinitride is decomposed into metallic barium and nitrogen, the metallic barium remaining disseminated through the nickel and the nitrogen being withdrawn by means of the vacuum pump. After the nitrogen has been removed, the temperature is increased to a red heat to cause the diffusion of the barium into the nickel. The slugs or briquettes thus formed were then worked into a wire by an alternate heating and swaging operation under conditions which prevent action between the alkali or alkaline earth metals and the furnace atmosphere. The heating may be performed in a vacuum or in an atmosphere which is inert with respect to the alkali or alkaline earth metals, such as helium or argon.

While I have described a specific embodiment of my invention, it will be understood that various modifications may be made therein without departing from the spirit of my invention. For example, an alkali or alkaline earth metal, or a mixture of two or more metals selected from either group, may be added to the ingredients of the alloy known as Konel, described in the copending application to Edwin F. Lowry, Serial No. 144,911, filed on October 28, 1926, which is assigned to the Westinghouse Electric & Manufacturing Company, and an improved alloy may be formed by my process which consists of the alkali or alkaline earth metals utilized, nickel, cobalt, iron and titanium. The alkali and alkaline earth compounds are added in such proportion that the resulting alloy will usually contain from 1 to 15 per cent of the alkali and alkaline earth metals. I prefer to utilize barium trinitrides or a mixture of barium and strontium trinitrides in the proportion of from 5 to 25%. Upon the decomposition of the trinitrides, the percentage of the alkali or alkalin earth metals, or a mixture of them, in the finished alloy, will not amount to more than 15%, the preferred proportion being from 5% to 10%.

Other modifications of my invention will be apparent to those skilled in the art and I desire, therefore, that only such limitations shall be imposed upon my invention as are required by the prior art and the appended claims.

I claim as my invention:

1. The process of producing an alloy between a metal having a compartively high melting point and a metal that is volatile at a temperature below 900° C. which comprises mixing the first named metal in a powdered state with a powdered compound of the volatile metal, pressing the mixture into the form of briquettes, heating the briquettes in a vacuum to decompose the compound of the volatile metal, and then heating the mixture to a sufficient temperature to cause the volatile metal to diffuse into the first named metal.

2. The process of producing an alloy between a highly refractory metal and a metal that is volatile at temperature below 900° C. which comprises mixing the refractory metal in a powdered state with a powdered compound of the volatile metal, pressing the mixture into the form of briquettes, heating the briquettes in a vacuum to decompose the compound of the volatile metal, and then heating the mixture to a red heat to cause the volatile metal to diffuse into the refractory metal.

3. The process of producing an alloy between one or more refractory metals and one or more metals selected from the metals of the alkali and alkaline earth groups which comprises mixing the refractory metal in a powdered state with a powdered compound of the last named metal, pressing the mixture into briquettes, heating the briquettes in a vacuum to decompose the alkali or alkaline earth compound, removing the gaseous products of decomposition, and then heating to a sufficient temperature to cause the volatile metal to diffuse into the refractory metal.

4. The process of producing an alloy between a refractory metal and an alkaline earth metal which comprises forming briquettes of a powdered mixture of the refractory metal and the alkaline earth trinitride, heating the briquette to decompose the alkaline earth trinitride, removing the nitrogen and any adsorbed gases, and then heating the mixture to a red heat to cause the alkaline earth metal to diffuse into the refractory metal.

5. The process of producing a barium-nickel alloy which comprises mixing barium trinitride in a powdered nickel, molding the powdered mixture and heating the molded product in a vacuum to a sufficient temperature to decompose the barium trinitride, withdrawing the nitrogen, and then heating the resultant mixture of barium and nickel to a sufficient temperature to cause the barium to diffuse into the nickel.

6. In the process of producing an alloy between at least one refractory metal and a metal selected from a group of metals consisting of the alkali and alkaline earth metals, the steps which comprise heating a briquette comprising an intimate mixture of the refractory metal and a compound of a metal selected from the alkali or alkaline earth metal groups to a sufficient temperature to decompose said compound, removing the gaseous decomposition products and heating the briquette to cause the metal selected from the alkali or alkaline earth metal groups to diffuse into the refractory metal to form an alloy.

7. In the process of producing an alloy between a plurality of refractory metals and a plurality of metals selected from a group of metals consisting of the alkali and alkaline earth metals, the steps which comprise heating a molded body comprising an intimate mixture of the refractory metals and compounds of the metals selected from the alkali or alkaline metal groups to a sufficient temperature to decompose said compounds, removing the gaseous decomposition products, and heating the briquettes to cause a diffusion of the metals.

In testimony whereof, I have hereunto subscribed my name this 14th day of August, 1928.

PORTER H. BRACE.