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NORMAN B. PILLING, OF WILKINSBURG, PENNSYLVANIA, ASSIGNOR TO WESTINGHOUSE ELECTRIC & MANUFACTURING COMPANY, A CORPORATION OF PENNSYLVANIA.

## SHAPED OXIDES AND METHOD OF PRODUCING THE SAME.

No Drawing.

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*To all whom it may concern:*

Be it known that I, NORMAN B. PILLING, a citizen of the United States, and a resident of Wilksburg, in the county of Allegheny and State of Pennsylvania, have invented a new and useful Improvement in Shaped Oxides and Methods of Producing the Same, of which the following is a specification.

10 This invention relates to the production of shaped oxides of various metals, more particularly metals of the alkaline and rare earths.

The present invention is capable of various adaptations and may be used for the production of various shaped articles, such as rods, wires, tubes, sheets and combinations thereof, for use as refractories, oxide-coated metal filaments, such as nickel, tungsten, molybdenum, platinum and the like, and for various other applications.

I have discovered that certain metals may be formed into a desired shape, the article thus formed being then oxidized, forming a tough, porous structure having a smooth surface which is capable of withstanding rapid temperature changes. Oxide articles containing or comprising oxides of various metals, such as the alkaline earth metals, of which calcium is an example, may be provided in the form of filaments which are characterized by their high thermionic emissivity when heated to temperatures at which tungsten is still inactive. This phenomenon renders such articles of considerable importance in radio-telegraphy.

My invention contemplates not only the forming of various articles entirely of oxides but contemplates also forming a metal article, the surface only of which has been oxidized to produce an integral, strongly adherent coating on the metal. Another aspect of my invention consists in coating a shaped article with a metal to any desired thickness and then oxidizing the surface coating only.

Coated articles, usually in the form of wires or filaments, are very desirable for use in thermionic vacuum tubes. It has been attempted to produce filaments of this kind by coating platinum filaments with an oxide, such as calcium oxide. This was accomplished by dipping the platinum filament in a solution of a calcium salt, for instance,

the nitrate, then drying the same, and redipping until the desired thickness of coating was obtained. The coated filament was then heated to a temperature sufficient to decompose the compound, leaving a film of oxide on the metal filament. Such filaments had their limitations. The process of forming the coating by dipping and baking was tedious and expensive, and the final product did not have a uniform coat. The oxide coating was not firmly united with the metal body and, very frequently, fell off in the form of scale, thus exposing the metal.

My invention contemplates a method of forming an oxide article by coating the metal with layers of oxide which are strongly adherent to the body of the article. In producing an article which is completely or partially converted into the oxide, I first form the same of metal into the shape desired and then place the article in a container and pass oxygen therethrough. I then apply heat to the container to cause a slow oxidation of the metal.

In providing a surface coating only on an article, I generally provide a base having the form of the finished article and made of a suitable metal, such, for example, as nickel, tungsten, molybdenum, or platinum. The article is provided with a coating of a metal, such as calcium, which is subsequently to be oxidized, in any suitable manner, as by electrolytic deposition, surface alloying, or condensation from metal vapor. The resulting metallic article is then oxidized as before to either partially or completely transform the metal coating into the oxide.

A specific example of the application of my new method to the formation of a refractory crucible is as follows: Metallic calcium is formed into a thin-walled crucible of the proper size and form which is placed in a container having a connection to a source of dry oxygen and an opening into the atmosphere. Oxygen is passed through the container slowly to displace such air as may be present. The container is then heated to a temperature of preferably 300 to 500° C., the atmosphere of dry oxygen being maintained. This causes a slow, complete oxidation of the metallic crucible without any change in the shape thereof, the final shape and size corresponding very

closely to that of the original metallic crucible. Care should be taken not to allow the temperature to rise materially above 500 or 550° C., in the case of calcium, since the metal ignites at such temperatures and burns, leaving the oxide in powdered or crumbly form.

The application of my process to the production of calcium-oxide-coated metal filament is as follows: Clean tungsten wire is uniformly covered with a coating of metallic calcium to the desired thickness by vaporizing metallic calcium and then condensing the same on the surface of the tungsten wire until a coating of the desired thickness is obtained. This duplex wire is now introduced into a heated furnace filled with dry oxygen at a temperature approximately 450° C. and is retained therein until the coating becomes completely oxidized. At the virtual completion of the oxidation, the last traces of calcium metal may be removed by raising the temperature and subjecting it to an oxidizing roast at a temperature limited by the nature of the metal base.

Another application of my process is the production of oxide-coated filaments for use in thermionic vacuum tubes. A difficulty in effecting this application has been the lack of a suitable means of preparing the initial calcium-metal coating, prior to conversion to oxide, of controlled thickness upon wires of small diameter.

I have succeeded in doing this by a process which consists in placing the object to be coated in a space (1) containing metallic calcium vapor and (2) which is simultaneously in a directed electrical field whereby the metal vapor is driven to the object and condensed on its surface. The means of realizing either of these two essential conditions is immaterial. The process is applicable to any metal with a vapor pressure sufficiently high to permit volatilization, irrespective of whether that metal coating is to be subsequently used as metal or chemically converted into an oxide or a salt.

Ordinarily, when a metal of the character utilized in my method is heated in air, it ignites and burns, often evaporating in part and leaving a powdery deposit of the oxide. The articles produced by my method have very desirable physical properties. They are strong mechanically and capable of withstanding considerable rough treatment, being flexible and resilient. They generally have smooth, glossy surfaces, are porous in texture, and are capable of withstanding rapid and great temperature changes. For instance, I have plunged cold articles formed by my method into an oxy-gas flame without causing any cracking.

Although I have described my invention specifically, illustrating the formation of crucibles and wire shapes of calcium oxide, it is apparent that my invention is not limited to such shapes or materials. For instance, I may use any of the alkaline-earth metals, such as barium or strontium, instead of calcium, I may utilize rare-earth metals and even others, for instance, copper, nickel, iron and the like. Furthermore my invention is not limited to the oxidation of metals as it is obvious that I may subject alloys to oxidation to form articles of mixed oxides.

It is not necessary in all cases to oxidize in an atmosphere of dry oxygen, this being utilized in the case of calcium because the nitrogen of the air combines with the calcium, and the water vapor causes a crumbly product. Other metals which do not combine with nitrogen may be oxidized in air. These and other changes in detail of manipulation will be readily apparent to those skilled in the art.

I claim as my invention:

1. A method of producing shaped articles which comprises forming said articles of a suitable metal and then slowly and completely oxidizing the same in an atmosphere of dry oxygen.
2. A method of producing shaped articles which comprises forming said articles of a suitable metal and then slowly and completely oxidizing the same in an atmosphere of oxygen.
3. A method of producing shaped articles which comprises forming said articles of calcium and then oxidizing the same.
4. A method of producing shaped articles which comprises forming said articles of calcium and then slowly oxidizing the same in an atmosphere of dry oxygen.
5. A method of producing shaped articles which comprises forming said articles of a suitable metal and then completely oxidizing the same in an atmosphere of dry oxygen.
6. A method of producing shaped articles which comprises forming said articles of an alkaline-earth metal and then oxidizing the same.
7. A method of producing shaped articles which comprises forming said articles of calcium and then oxidizing the same at a temperature less than 550° C.
8. Shaped articles consisting of an oxide of calcium which is adherent and mechanically strong.

In testimony whereof, I have hereunto subscribed my name this 4th day of December 1920.

NORMAN B. PILLING.