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AGGLOMERATED MATERIAL IN PARTICULAR FOR ELECTRICAL PURPOSES AND SHAPED BODIES MADE THEREFROM

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This invention relates to an agglomerated material, in particular for electrical purposes, and shaped bodies made therefrom. The invention further comprises a process of manufacturing such material and bodies.

This application is a continuation in part of my copending application Ser. No. 681,397, filed July 20, 1933, and issued into Patent No. 2,096,924 which is in turn a continuation in part of my previous copending application Ser. No. 594,154 filed February 19, 1932, and issued into Patent No. 2,030,229.

It has been proposed to make such agglomerated material and shaped bodies, in particular for electrical purposes, of different metals, such as tungsten and molybdenum on one hand and gold, silver, copper, iron, nickel, platinum, aluminum, tin and zinc on the other hand. The higher melting and more refractory metal of the first group in a finely powdered state as derived from its ores, or compounds, has been mixed with the lower melting material of the second group, and the latter has been melted so that it compounded with the higher melting material upon cooling.

It has also been proposed to unite tungsten powder by low sintering into a spongy coherent body, and to cause it to absorb melted copper which upon cooling fills the pores of the spongy tungsten body.

According to this invention an agglomerated material, in particular for electrical purposes, and shaped bodies adapted for electrical contacts or the like is also manufactured of metal taken from two groups. The first group consists of tungsten, molybdenum and tantalum which are highly refractory metals of high melting point and well suited as contact material. They do not easily melt under the heat of an arc developed between the contacts of a switch when it is opened. They are however of low electrical conductivity and oxidize easily when heated to high temperature for a more extended period of time. The second group of metal comprises silver, copper, nickel, cobalt, iron, gold, chromium, aluminum, tin, zinc, platinum which are of considerably higher conductivity than those of the first group, or which do not oxidize as easily as the metal of the first group does. In particular, the metals of the second group do not mix or alloy with those of the first group.

Some of the metals of the second group do not mix under any condition and some of them do not mix if the metal of the first group remains solid during agglomeration.

However, according to this invention, the metals of the first group are not taken in the finely powdery state in which they are obtained from their ores or compounds, but are artificially provided with a larger volume in comparison with their surface area. In other words, the metal of the first group is applied in particles which are coarser than those of the original metal powder obtained from its compounds or ores. By increasing the volume in comparison with the surface area, the resistance against attacks of oxygen in the surrounding air, also at elevated temperatures, is considerably increased. Furthermore, the metal powder is rendered ductile and the agglomerated bodies made therewith can be more readily worked and shaped.

A preferred process of the invention consists in that the tungsten-, molybdenum- or tantalum-powder, as it is obtained from the ores or compounds is first compacted by heat treatment at temperatures at least as high as sintering temperature whereby a sintered or melted solid body of these metals is obtained which is then comminuted to particles of a size coarser than the original metal powder. The sintered or melted metal bodies may also be worked, in particular rolled or hammered before they are comminuted.

In any case, the coarser particles obtained are more ductile than the original powder, and they are, due to their smaller surface area, compared to the volume enclosed, and due to their larger diameter, more resistant to corrosion by the electrical arc and the oxygen of the air, if the contacts are heated by the arc. The coarse powder thus obtained is uniformly and finely crystalline.

The agglomerated material or shaped bodies may then be made in the following way.

The coarser powder may be mixed with powdery metal taken from the second group and preferably pressed. Thereupon the body is heated to a temperature at which all the lower metal present melts, but below a temperature at which the coarser metal taken from the first group could change its structure, in particular soften, sinter or melt.

Thereupon the body is permitted to cool, or cooling is caused in any desired way, if the structure of the lower melting metal is to be affected. Pressure may be applied, if desired, during this, or any other consolidation process covered by this invention. The final body may have the shape of a bar, or rod, from which the desired contacts or other articles may be cut, sliced, or obtained by any other mechanical or even thermal treatment. (The latter consists in reheating the body into a plastic or molten state of the lower melting metal

contained in the body). The final body however shaped in a suitable mould may already have the desired shape.

Another process for arriving at the products according to this invention consists in shaping the coarser powder taken from the first group and to apply pressure to it, and then to pour over it fused metal taken from the second group which infiltrates into the pores of the shaped body of metal of the first group and agglomerates upon cooling. Again cooling can be performed according to any chosen metallurgical rule.

In addition to the metals taken from the first and the second group titanium may also be used which is known as a deoxidizing agent. It has to be present in addition to at least one metal of the first and one metal of the second group. The amounts of the metal to be taken from the second group depend upon the effect desired. The metal of the second group may amount to about 3% to 6% and up to 15%, if it has to act merely as a binder, whereas it may be present in amounts up to 97%, if it is to act as electrically conducting material in the contact itself.

Titanium, if added, may be used in quantities of about 3% to 6%, up to 15%.

The agglomerated body thus obtained has proven in practice to have exceptional qualities. Due to the presence of tungsten, molybdenum, or tantalum in a coarser state it is more resistant against mechanical wear and deformation during use, for instance as contact in a switch which is to be closed quickly and forcibly. The quasi ductilised coarse particles will better resist the impact of heavy strokes when the switches are closed. Due to the presence of lower melting, but in general better conducting metal, the contact will not be heated as high by the current passing the closed switch as it is the case when tungsten etc. alone is used. Thereby the tendency of the contact to oxidize when the switch is closed is considerably reduced, because the temperature to which it is heated is lower than it would be if the contact consisted of tungsten etc. alone. Furthermore, such a body can easily be connected with a support by soldering at lower temperature, at which the low melting metal present can be soldered, whereas soldering of tungsten alone to any support is very difficult, due to the fact that it is not wetted by most of the metals. Furthermore, due to the low temperature applied during the soldering or brazing operation it can be performed in open air and, in general, without protecting gaseous atmosphere, and no oxidation of the body will occur due to this low temperature and the greater resistivity of the coarse metal particles against the attacks of the oxygen of the surrounding air. The fact that the lower melting metal does not mix with the higher melting one is important because the low melting metal thus keeps its low melting point and its good brazing and soldering qualities which would be affected however if an alloy were formed between that metal and tungsten. Such alloy would be of considerably higher melting temperature than that of the lower melting metal and the properties of the alloy would essentially differ from those of the low melting component, as far as e. g. soldering and brazing qualities are concerned.

Even if the low melting metal is not of higher conductivity than tungsten or molybdenum, as it is the case with tin and zinc, nevertheless, the extremely low melting point of those metals and their low oxidation properties aid in effecting a perfect connection with any support in particular of the same metal, excluding any oxidation of the tungsten particles.

Contacts of this type may be connected with a support of e. g. copper, aluminum, chromium, silver, tin, zinc which may either be rigid, or elastic like springs.

The following examples of binary composite bodies corresponding to the invention may be given:

Molybdenum-silver; molybdenum-chromium; molybdenum-copper; molybdenum-tin; molybdenum-zinc. Tantalum-copper; tantalum-aluminum.

Tungsten-silver; tungsten-chromium; tungsten-copper; tungsten-tin; tungsten-zinc; tungsten-aluminum.

The following examples of ternary structural composite materials may be given:

Molybdenum-silver-chromium; molybdenum-silver-titanium; molybdenum-chromium-titanium; molybdenum-chromium-copper; molybdenum-chromium-tin; molybdenum-chromium-zinc; molybdenum-copper-titanium; molybdenum-nickel-copper.

Tantalum-aluminum-titanium.

Tungsten-silver-titanium; tungsten-chromium-titanium; tungsten-copper-titanium; tungsten-tin - titanium; tungsten - zinc - titanium; tungsten - silver - chromium; tungsten - copper chromium; tungsten-nickel-copper.

For making the material or bodies the process may be to pour the melted and therefore liquid lower melting metal over the compact high melting metal powder. However, parts of the lower melting metal in solid form, more particularly in the form of powder, may be added to and intimately admixed with the powdered higher melting metal, and the whole may then be cast over with the remainder of the lower melting metal, which, however, is fused. In this case the whole is preferably maintained at a temperature such that the admixed lower melting metal powder melts as well and becomes incorporated with the lower melting metal which is cast on.

Finally, the procedure may also be such that both the higher melting and lower melting metals are comminuted, mixed and the whole thereupon heated to such an extent that at least the lower melting metal melts and incorporates the higher melting metal on cooling, which latter will become uniformly distributed in the solidified metal.

In these ways in the first place whole blocks or bars can be obtained of any shape or size, which are homogeneous throughout and from which the desired article can be made by heat treatment, e. g. recasting, or by mechanical working in the hot or cold, such as hammering, rolling, drawing, cutting, slicing.

The material obtained in this way may be mechanically worked; more particularly it may be extended by hammering or rolling and the sheets obtained punched and pressed.

It is also possible to obtain the desired article direct by inserting the metal powder mixture into a suitable mould and bringing the lower melting metal portion in it to fusion so that it takes up the higher melting metal part during cooling and imparts great homogeneity and uniform density to the body being made.

Frequently, however, it is desired to make only certain parts of the body according to the invention, i. e. to make a composite body, such as, making a contact pin in which case only the

outer contact surface is to be hard and resistant to heat and oxidation, whilst the remaining part may not have the same resistance capability as the contact surface. In such a case the procedure is preferably such that a mould open at the top is used, the lowest part of which is adapted to the contact surface, on which the higher melting metal powder is applied in sufficient layers, after which the lower melting metal is poured or fused thereon, care naturally being taken that no air bubbles are entrained and consequently the casting is preferably carried out in a mould with discard head and in such a way that slow cooling which progresses from the bottom to the top is effected. A contact is then obtained which contains the higher melting metal at the contact surface and which possesses the desired general properties.

Similar results can also be attained by choosing the metals according to their density and taking care that the metal bath in which the lower melting metal is fluid and the heavier high melting metal is solid, remains in the hot liquid state for a certain time, as a result of which the heavy metal powder can slowly move downwards and the bath is at least enriched in heavier high melting metals or metal powders in the lower part thereof, whereupon the bath is allowed to set.

It is always possible to add the high melting metal not only in the form of ductile powder but also in other form as short or long wires which have been bundled or laid and which consequently have already been rendered compact and ductile during their preparation by hammering, drawing and so forth. These bodies can then be enclosed or melted around by the desired lower melting metal as a result of which a composite body is attained from which the desired articles can be made. Thus it is possible to cast a lower melting metal (or metal mixture) cylindrically around such a cable or the like of tungsten or molybdenum wire. This can be more particularly carried out in a continuous process, such as in machines for pressing the soft metal about the hard and thin plates, or longer, somewhat cylindrical composite bodies which are used, as contact bodies. In these the wires of tungsten or molybdenum are then incorporated so that the electric current advantageously flows in the direction of the "fibre" of the wire.

When the composite body is made in the said manner in a machine for pressing one metal around the other, the lower melting metal is united to the harder metal in the hot liquid state or at least in a plastic state produced by heating. Production is effected, therefore, both in the hot state and under raised pressure which can be increased in individual cases to between 25 atm. and 50 atm. and even above.

The finely crystalline structure of the composite body sets in of itself, the higher melting metal obtained by melting or highly sintering either already possessing such structure or else acquiring it subsequently by mechanical working. If necessary, however, a particularly desired finely crystalline structure may be obtained by thermal treatments such as known per se in the metal working art, thus, for example, by rapid cooling or chilling of the composite body during the manufacture or by subsequent heating of the ready made article or body and subsequent rapid cooling thereof.

It is a well-known fact that the union of higher melting metals like tungsten and molybdenum with other bodies offers difficulties. Such bodies of high melting point are frequently chosen since they can be heated to a higher temperature during use, and the union with a support must then be effected with the aid of a hard solder. As a rule when soldering undesirable oxidation appears on the tungsten etc. body. For many purposes also tungsten, etc., bodies are required having a compact surface (high lustre) which offers resistance to corrosion. Such compact bodies, however, can be produced only by mechanical working, for example, by rolling out tungsten sheets of extraordinary thinness. If now bodies are shaped or cut from such sheets and united with other bodies by means of hard solders, then merely the compact skin is lost by oxidation.

According to the invention sheets of tungsten, molybdenum and so forth, are made of the desired thickness, and also sheets of a conglomerate of the kind above described, e. g. of copper-tungsten, and these two sheets are layed one upon the other and united in the hot, advantageously in a reducing atmosphere and by mechanical pressure. The sheets blend together and a unitary sheet is obtained which consists of tungsten on one side and of copper-tungsten on the other side. However, copper-tungsten is easy to solder. In addition the tungsten on the copper-tungsten side can be dissolved out, e. g. by etching with potassium nitride, so that a sheet is obtained which consists of tungsten on one side and to a greater or less extent of pure copper on the other side. The union between these two parts is extraordinarily intimate and they cannot be separated either during subsequent working or during operation. No perceptible electrical transition resistance can be detected, nor is it to be expected since non-conducting oxides are absent.

The procedure may also be such that a sheet of copper-tungsten is laid on a tungsten sheet of any desired thickness or thinness and on top of the same a sheet of copper is placed, and the three sheets are united to a three-fold sheet in the hot and in a reducing atmosphere and preferably with employment of a suitable pressure. Once again the copper-tungsten is intimately and inseparably united both with the tungsten and with the copper. In this case the chemical treatment of the copper-tungsten for the purpose of dissolving out the tungsten is dispensed with. This latter process is frequently of advantage since pores are formed in the copper owing to the dissolution of the tungsten which are desirable for soldering purposes.

A further method consists in rolling out a block of copper-tungsten prepared as being described above and which consists for the most part of tungsten on the one side and on the other side for the most part or exclusively of copper in the direction of the layers whereby a sheet is obtained which on one side consists for the most part or exclusively of tungsten and on the other side for the most part or exclusively of copper. A tungsten sheet can be united with this sheet on the side consisting for the most part of tungsten in the manner previously described, should the sheet not be forthwith suitable for the purpose in view.

Sheets obtained in this way may be of any desired thickness or thinness; the thickness of three-fold sheets can always be considerably less than 1 mm. since the individual sheets can be rolled out to thicknesses amounting to a fraction of a millimetre (e. g. $\frac{1}{10}$ mm.).

If electric contacts are stamped out of such a sheet then these can be united with the support, e. g. iron or aluminum spring, by soft soldering,

all oxidation and structural change in the joined part being excluded. Sheets obtained in the said way may also be coated with tin on the copper side, or a sheet of tungsten-copper-tin may be made first of all when the soldering is particularly facilitated and soldering temperatures of 230° C. and less may be employed. No oxidation nor impairing of the mirror-smooth highly lustrous rolled surface of the tungsten can take place, which latter surface on account of its great compactness is substantially more resistant to corrosion and oxidation than the surfaces of known contacts. If, however, as has been frequent hitherto, the contacts must be hard soldered with nickel or nickel alloys or even welded then oxidation of the tungsten-body is unavoidable, the compact rolled surface disappears and of course the contact surface cannot be produced again even by subsequent rubbing with emery or polishing. It is obvious that by such heat treatment steel springs or special alloys which rust only with difficulty are impaired. In addition the expedient of welding the tungsten contact on to an iron base first of all which in turn is united with the support has, quite apart from its cost, afforded no permanent help.

A further advantage of the invention, however, consists in this that contacts can now be made from the thinnest sheet tungsten, which is made of a thinness approaching that of a skin (about $\frac{1}{10}$ mm. thick) and united to the support by means of soft soldering with the aid of the connecting layer. This expedient can be adopted in all cases in which particular heating does not arise during the operation, as, for example, in the case of telephone contacts, (more particularly for contact springs in automatic telephony) which must not oxidise and must occupy as little space as possible.

Double or multi-layered sheet made in the manner described can also be pressed in an astonishing manner in the cold or under conditions of slight heat. Obviously the thin tungsten sheet is made more shapeable (i. e. plastic) owing to its ideal union with the still more ductile copper-tungsten sheet. A body made in this way can then be used as such or after removal of the copper by chemical means (dissolution in nitric acid). The tungsten skeleton remaining after dissolution of the copper can then be rubbed down, scraped off or ground off. In this way it is possible to make even complicated articles of tungsten, molybdenum and so forth, such as, for example, calottes or bodies of revolution, such as hitherto for many purposes (Röntgen electrodes) could be made only at much cost and trouble by difficult casting operations.

It may be said in general that the invention enables either difficulty melting or hard bodies to be coated more particularly plated, with low melting or softer bodies to any desired thickness on one or both sides, or vice versa low melting or soft bodies to be coated or plated with higher melting or harder bodies on one or both sides. The union is in every case effected in the heat with suitable mechanical pressure and absence of oxidising agents.

The invention is not in any way limited to the procedure set forth in the examples given. It may be used, for example, for lcom motor switches which as is well known are subjected to a very great mechanical wear. The contact of such a switch has approximately a double T-cross section and according to the invention is made for the most part from a copper rod which is provided on one side with a layer of copper-tungsten and is then drawn or rolled into the desired section, so that a copper rail is obtained which has one surface of copper-tungsten and from which a contact of the desired length can be cut off. In a similar way, from round copper rods which are coated completely with a copper-tungsten layer it is possible to draw tubes or wires which consist on the exterior of copper-tungsten and in the interior of copper.

Although here conglomerate bodies of any desired shapes, such as wires, and sheet, consisting of tungsten and copper have been more particularly described, yet the process may be employed to every other conglomerate body such as has been set forth in the introduction. Thus, for many purposes aluminum bodies with tungsten or molybdenum layers, as well as copper bodies with tungsten layers, are to be recommended.

What I claim is:

1. An agglomerated material, in particular for electrical purposes, and shaped bodies made therefrom, consisting of at least one metal selected from a first group consisting of tungsten, molybdenum and tantalum, and at least one metal selected from a second group consisting of silver, nickel, cobalt, iron, copper, aluminum, gold, chromium, tin, zinc, platinum, the metal of said first group present in individual dense particles coarser than those of the original metal powder obtained from its compounds or ores, and obtained in such coarser state by heat treatment at temperatures at least as high as sintering temperature and subsequent powdering, the metal of said second group forming substantially a solidified melt agglomerating said individual coarse particles and present in amounts of about 3% to 90% of the material or bodies.

2. An agglomerated material, in particular for electrical purposes, and shaped bodies made therefrom, consisting of at least one metal selected from a first group consisting of tungsten, molybdenum and tantalum, and at least one metal selected from a second group consisting of silver, nickel, cobalt, iron, copper, aluminum, gold, chromium, tin, zinc, platinum, the metal of said first group present in a fibrous state comminuted to dense particles coarser than those of the original metal powder obtained from its compounds or ores, the metal of said second group forming substantially a solidified melt agglomerating said particles and present in amounts of about 3% to 90% of the final material or bodies.

3. An agglomerated material, in particular for electrical purposes, and shaped bodies made therefrom, consisting of at least one metal selected from a first group consisting of tungsten, molybdenum and tantalum, and at least one metal selected from a second group consisting of silver, nickel, cobalt, iron, copper, aluminum, gold, chromium, tin, zinc, platinum, and an admixture of titanium in an amount of about 3% to 15%, the metal of said first group present in particles coarser than those of the original metal powder obtained from its compounds or ores, the metal of said second group forming substantially a solidified melt agglomerating said particles, containing said admixture and being present in amounts, including said admixture, of about 6% to 90% of the final material or bodies.

4. A process of manufacturing an agglomerated material for electrical purposes and shaped bodies therefrom, containing at least one metal selected from a first group consisting of tungsten, molybdenum, tantalum, and at least one metal

selected from a second group consisting of copper, aluminum, gold, chromium, tin, zinc, platinum, said process consisting in first compacting metal taken from said first group in its initial powdery form in which it is obtained from its compounds or ores by heat treatment at temperatures at least as high as sintering temperature, then powdering the so compacted metal to particles coarser than those of the initial powder and mixing it with metal taken from said second group, and thereupon consolidating this mixture by heat treatment at temperatures below the sintering temperature of said first group metal.

5. A process of manufacturing an agglomerated material for electrical purposes and shaped bodies therefrom, containing at least one metal selected from a first group consisting of tungsten, molybdenum and tantalum and at least one metal selected from a second group consisting of cobalt, iron, aluminum, gold, chromium, nickel, tin, zinc, platinum, said process consisting in first compacting by heat treatment initial metal taken from said first group in the powdered form in which it is obtained from its compounds or ores at temperatures at least as high as sintering temperature, then mechanically working the compacted metal, then powdering the so compacted metal to particles coarser than those of the initial powder and mixing it with metal taken from said second group, thereupon heating this mixture at a temperature at least sufficiently high to melt the metal taken from said second group but below a temperature at which the structure of the metal of said first group is materially changed.

6. A process of manufacturing an agglomerated material for electrical purposes and shaped bodies therefrom, containing at least one metal selected from a first group consisting of tungsten, molybdenum, tantalum, and at least one metal selected from a second group consisting of silver, nickel, cobalt, iron, copper, gold, aluminum, tin, zinc, chromium, platinum, and an admixture of titanium in an amount of about 3% to 15%, said process consisting in first compacting metal taken from said first group in its initial powdery form in which it is obtained from its compounds or ores by heat treatment at temperatures at least as high as sintering temperature, then powdering the so compacted metal to particles coarser than those of the initial powder and mixing it with metal taken from said second group and said admixture, and thereupon consolidating this mixture by heat treatment at temperatures below the sintering temperature of said first group metal.

7. A process of manufacturing agglomerated shaped bodies for electrical purposes containing at least one metal selected from the first group consisting of tungsten, molybdenum, tantalum, and at least one metal selected from a second group, consisting of silver, nickel, cobalt, iron, aluminum, gold, chromium, tin, zinc, platinum, said process consisting in first compacting metal taken from said first group in its initial powdery form in which it is obtained from its compounds or ores by heat treatment, at temperatures at least as high as sintering temperature, then powdering the so compacted metal to particles coarser than those of the initial powder, shaping the powder formed of said particles and thereupon pouring thereover melted metal taken from the second group, and cooling the agglomerated body thus obtained.

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