Dec. 12, 1939. C. J. SMITHELLS 2,183,359

METHOD OF MANUFACTURE OF HEAVY METALLIC MATERIAL

Filed March 22, 1939

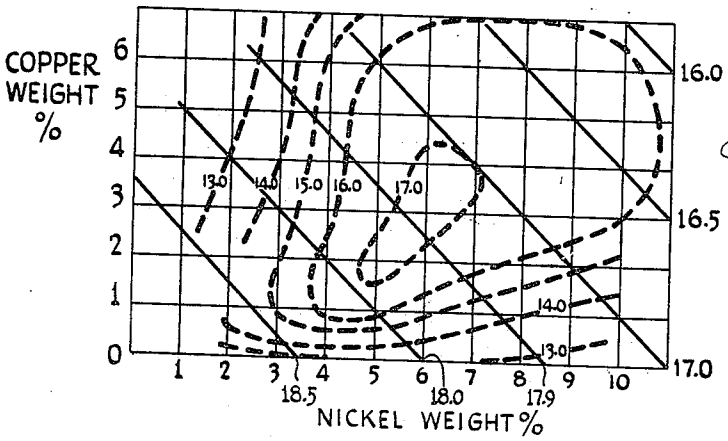


Fig. 1.

Fig. 2.

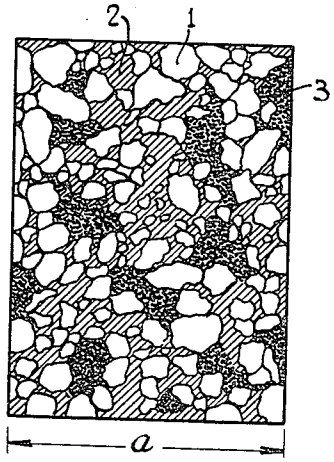
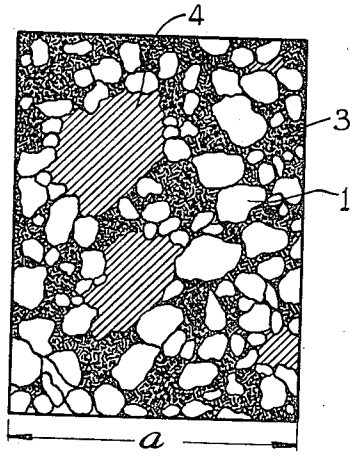


Fig. 3.



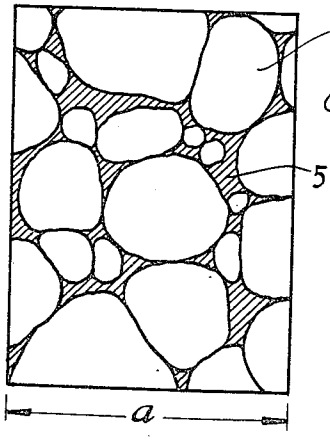


Fig. 4.

INVENTOR
COLIN JAMES SMITHELLS
BY
ATTORNEY

Patented Dec. 12, 1939

2,183,359

UNITED STATES PATENT OFFICE

2,183,359

METHOD OF MANUFACTURE OF HEAVY METALLIC MATERIAL

Colin James Smithells, Rugby, England, assignor to The General Electric Company Limited, London, England

Application March 22, 1939, Serial No. 263,388
In Great Britain June 24, 1938

6 Claims. (Cl. 75—22)

This invention relates to the manufacture of the new metallic material, described in my co-pending application No. 220,209, which is composed of tungsten, nickel and copper, has a density of not less than 16 gm./ml., and consists of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimetre of section of the material.

The object of the invention is to provide a process, which is a modification of that described in British patent specification No. 447,567, for producing the said material by means of which a given density of the material may cheaply be obtained.

The invention will now be described in detail and reference will be made to the accompanying drawing in which

Figure 1 shows curves relating the composition of the new material to its density,

Figures 2 and 3 show microscopic views of etched sections of known metallic materials produced by the process described in the said British patent specification No. 447,567 and

Figure 4 shows a microscopic view of an etched section of an example of the new metallic material produced by the method in accordance with the invention.

In the process described in the said British patent specification a compressed mixture of fine tungsten powder and fine powder of nickel and/or copper is heated to a temperature not exceeding 1500° C.

If in carrying out this process the starting materials consist of tungsten and copper powders only, without nickel, the resulting metallic material always consists of the original tungsten particles, not greatly increased in size and preserving their original angular shape, cemented together by copper, which does not fill all the space between the particles.

This structure is illustrated in Figure 2; the dimension marked *a* corresponds to about 0.11 mm. In this figure, 1 are tungsten grains, 2 the cementing copper, 3 voids. Such a structure is to be expected; for it is known that molten copper, while it wets tungsten, does not alloy with it at temperatures below 1500° C.

On the other hand, if the starting mixture contains nickel, which when molten dissolves tungsten, the tungsten particles in the resulting alloy tend to be substantially larger and more nearly spherical than the original particles. Apparently the small tungsten particles dissolve in the nickel and the larger particles grow by taking up tungsten from the solution. But if nickel is present without copper, the growth of the tungsten particles is apt to be limited, at least if they are not originally very small; the nickel (in which is dissolved some tungsten) is apt to collect in large pools and not to penetrate between the tungsten particles. This structure is illustrated in Figure 3, where the dimension marked *a* again corresponds to about 0.11 mm. Here 1 are the tungsten grains, 4 the nickel pools, 3 the voids.

I have now found that if both nickel and copper are present in suitable proportions and coarse tungsten powder is used in the starting mixture, the growth of the tungsten particles is much more pronounced and the molten nickel-copper-tungsten alloy penetrates freely between them. This effect of the copper is probably due to its reducing the melting point (especially when the sintering temperature is near the melting point of nickel) and surface tension of the molten material.

Thus in my method I make an intimate mixture of nickel powder, copper powder and coarse tungsten powder; I form from this mixture by means of pressure a self-supporting body and I then sinter this body until the new metallic material is formed.

The resulting new metallic material is a complex of nearly spherical tungsten grains, much larger than the original particles, cemented together by a nickel-copper-tungsten alloy, almost without voids. This structure is illustrated in Figure 4, where the dimension marked *a* is again about 0.11 mm. Here 1 are the large tungsten grains, 5 the nickel-copper-tungsten alloy filling completely the spaces between them.

Structures intermediate those of the known metallic material shown in Figures 2 and 3 and the new metallic material shown in Figure 4 may be produced. Thus, if the time or temperature of sintering is too small, a structure intermediate between that of Figures 2 and 4 may be produced, even if both nickel and copper are present. With the new material the theoretical density is attained more nearly than with the known materials having structures as shown in Figures 2 and 3. While it is possible to attain, or approach very nearly, the theoretical density in a material containing no copper by reducing the voids in a structure of the kind shown in Figure 3 by increasing the time and temperature of the sintering it is much easier and cheaper to attain the theoretical density, or a given fraction of it, with the new material produced by the method in accordance with the invention.

The theoretical density means the density calculated from the proportions and densities of the components (that is to say, 19.3 for tungsten, 8.9 for copper or nickel) on the assumption that there are no voids and no interpenetration. Since no interpenetration appears ever to occur, the theoretical density is the maximum density that a material of given composition can attain. Of course every theoretical density is not greater than any non-theoretical density; for the theoretical density depends on the composition. Thus a material containing 12% of (copper+nickel) which has the theoretical density 16.9 is less dense than one containing 4% of (copper+nickel) and having only 91% of the theoretical density 18.4. Nevertheless it is desirable that metallic materials of the kind referred to should have as nearly as possible the theoretical density; for at a given density, deficiency from the theoretical density means more tungsten (which is the expensive constituent) and also usually less desirable mechanical properties.

Materials that contain copper without nickel, and more than 83% tungsten, never attain substantially theoretical density, however great the proportion of copper and however long the period of sintering; for it appears that voids can be filled up only by the process of solution and growth that leads to the large-grain structure. On the other hand materials containing nickel and copper in sufficient quantity, and in proportions adapted to promote the formation of the large-grain structure characteristic of the new material produced by the method in accordance with the invention, attain quickly densities 95% of the theoretical, and in practicable conditions may attain 98%.

The limits of composition within which the new material can be produced by the method in accordance with the invention depend mainly on three factors, namely (1) the grain size of the coarse tungsten powder, (2) the temperature at which the mixture is sintered, (3) the time for which it is sintered. The pressure by which the material is compressed before sintering is relatively unimportant, so long as it is sufficient to form a self-supporting body; 5 tons per sq. in. has always proved sufficient. The self-supporting body shrinks greatly (e. g., about 20% in linear dimensions) during sintering. Here it is to be noted that, in the manufacture of the new material by this process, the temperature must never be so high that the body collapses and loses its shape; this is implied by the term sintering. The grain size of the copper and nickel is also unimportant, so long as it is not much greater than that of the tungsten. The surrounding atmosphere during sintering must be neutral or, preferably, reducing; but there appears to be no difference between pure hydrogen and a non-explosive mixture of hydrogen and nitrogen.

I will now proceed to describe with reference to Figure 1, the facts regarding composition for one particular choice of the factors (1), (2), (3). In the experiments to which this figure refers, the tungsten powder has 35% of its particles less than 2μ in diameter and substantially none greater than 8μ in diameter; such a powder is considerably coarser than that now generally used as a starting material for making tungsten lamp filaments, and is considerably cheaper.

The mixtures were all sintered at 1450° C. for one hour. It will be realised by those skilled in the art that this account of the grain size does not identify the powder completely; but it is difficult to describe the grain size in any manner that does identify it completely. Accordingly, since the time and temperature of heating necessary to obtain a given result varies with the grain size, it is not asserted that the results about to be described will be obtained with any powder having a grain size within the said limits. All that is essential is that there is a powder, having a grain size within these limits, from which the results about to be described can be obtained by heating to 1450° C. for one hour; and that the results can be obtained from any powder having a grain size within these limits, if the time and temperature of heating are adjusted to a value not very different from those given. Here it may be observed that it is not easy to measure a furnace temperature of 1450° C. by commercial methods with an error much less than 25° C.; accordingly 50° C. is not to be regarded as a large difference.

In the figure the abscissae are the percentages of nickel, the ordinates the percentages of copper; the remainder is always tungsten. (Percentages, here and everywhere, are percentages by weight.) The straight lines crossing the diagram from left-top to bottom-right denote, by the numerals marked against them, the theoretical densities of the compositions through which they pass. The dotted lines denote, by the numerals marked against them, the actual densities of the compositions through which they pass. Compositions not on a dotted line give, of course, densities intermediate between those marked on the dotted lines between which they lie; those inside the line marked 17.0 have densities not less than that figure.

I have found that all those compositions that lie on or inside the line marked 16.0 have the characteristic structure of the new metallic material.

It will be seen from the diagram that

(1) The new metallic material almost always has substantially more nickel than copper; the nickel content always lies between 4 and 11% and the copper content between 1 and 6%.

(2) With 5% of nickel and 5% of copper the new material just has a density of 16; with 5% of nickel and no copper the material produced by the process described has a density of less than 14 and has not the structure characteristic of the new metallic material.

(3) The new metallic material almost always has a density less than the theoretical; but, when the proportion of copper and nickel in an alloy is suitable, the deficiency may be only 2%.

(4) The maximum density is in the neighbourhood of 6% nickel and 3% copper.

However it should be noted that density per se may not always be the only consideration. Tensile strength and ease of machining may be important. These qualities are determined almost wholly by density and are practically independent of composition, density being constant. Machinability decreases generally as density increases, so that a compromise may have to be made. But the variation is not large. The new material of density 16 has a Brinell hardness of some 220, that of density 17 a hardness of 290; both can be machined without serious difficulty. The composition that my experiments indicate to be the best for most purposes is 6.4% nickel and 2.6% copper.

The statements just made with reference to the figure are true only if the grain size, temperature and time of heating are as aforesaid. I

will now explain how they are to be modified if these factors are changed.

It may be said broadly that decrease of particle size, increase of temperature, and increase of time of heating are equivalent, and that the effect of any one of them or of all in combination is to increase the area enclosed within any given dotted curve, (and so the range of compositions within which any given density can be obtained) subject, of course, to the condition that a curve can never cross the straight line similarly marked. With extension of the area corresponding to densities above a given limit goes, in general, extension of the area within which the new material may be obtained.

Again, if the grain size to which the figure refers is used, but the temperature increased to 1500° C. for 1 hour, the area within which the new material may be obtained is again increased. For, since the final equilibrium is attained more nearly, the new material will attain more nearly the theoretical density.

Increase of time produces much the same effect as increase of temperature; but the increase has to be considerable. Thus an increase of the time of sintering from 1 to 6 hours is approximately equivalent to an increase of temperature from 1450° C. to 1500° C.

Conversely, a diagram very similar to Figure 1, though not entirely identical with it, would result from decreasing the particle size and decreasing also the time or temperature of sintering. If the powder is fine enough and the time of sintering long enough, such a diagram could be produced at a temperature as low as 1400° C., or even lower.

On the other hand if much coarser powder was used, considerably greater temperatures or times would be necessary to obtain the new material. The particle size of the powder to which the figure refers is not far from the coarsest that can be used economically.

Considerable enlargement of the curves of the figure is not practically desirable. For finer powder, higher temperature and longer period of sintering all increase the cost of manufacture; while the rise in the maximum density obtainable is not nearly so marked as increase in the range of compositions over which a given density, and especially a very high density such as 17, can be obtained. It is therefore desirable to limit the fineness of the powder, the temperature and the time of heating. In virtue of what has been said such a limit can be imposed in practice by limiting the compositions of the new material; for, though it is possible to use more expensive methods than are actually necessary, these are not likely to be employed. The limits chosen may be somewhat wider than those indicated in the figure; for a slight enlargement of the curves does not involve any considerable extra expense. The limits of composition may then be taken to be ½–13½% of copper, 3½–16½% of nickel, and 83–96% of tungsten.

I claim:

1. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimeter of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture lying within the range 3½–16½% of nickel, ½–13½% of copper and 83–96% of tungsten, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body until said new metallic material is formed.

2. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimeter of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture lying within the range 3½–16½% of nickel, ½–13½% of copper and 83–96% of tungsten, and wherein not more than 35% of the tungsten grains in the mixture are less than 2μ in diameter and the remainder of the tungsten grains are between 2μ and 8μ in diameter, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body until said new metallic material is formed.

3. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimetre of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture lying within the range 3½–16½% of nickel, ½–13½% of copper and 83–96% of tungsten, and wherein not more than 35% of the tungsten grains in the mixture are less than 2μ in diameter and the remainder of the tungsten grains are between 2μ and 8μ in diameter, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body at about 1450° C. for about 1 hour.

4. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimetre of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture being 6.4% of nickel, 2.6% of copper and 91% of tungsten, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body until said new metallic material is formed.

5. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimetre of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture being 6.4% nickel, 2.6% of copper and 91% of tungsten, and wherein not more than 35% of the tungsten grains in the mixture are less than

2μ in diameter and the remainder of the tungsten grains are between 2μ and 8μ in diameter, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body until said new metallic material is formed.

6. The method of manufacturing a new metallic material composed of tungsten, nickel and copper, said material having a density of not less than 16 gm./ml. and consisting of large grains of tungsten cemented together by a tungsten-nickel-copper alloy, there being not more than 1500 grains of tungsten per square millimetre of section of the material, which comprises the processes of forming an intimate mixture of nickel powder, copper powder and coarse tungsten powder, the composition by weight of the mixture being 6.4% of nickel, 2.6% of copper and 91% of tungsten, and wherein not more than 35% of the tungsten grains in the mixture are less than 2μ in diameter and the remainder of the tungsten grains are between 2μ and 8μ in diameter, subjecting said mixture to pressure so as to form a self-supporting body and sintering said body at about 1450° C. for about 1 hour.

COLIN JAMES SMITHELLS.