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Schladitz

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[54] **METHOD OF MANUFACTURE OF MATERIALS FROM POLYCRYSTALLINE FILAMENTS**

[76] Inventor: **Hermann J. Schladitz,** Bodenseestr. 3a, Munich, Germany

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[63] Continuation of Ser. No. 31,022, Aug. 22, 1970, abandoned.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **C23c 11/02**

[58] **Field of Search** .... 117/107.2 R, 130 E, 117/65.2, 71 M; 75/208; 29/419, 420

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Primary Examiner—Alfred L. Leavitt
Assistant Examiner—J. Massie
Attorney—Kane, Dalsimer, Kane, Sullivan & Kurucz

[57] **ABSTRACT**

A process for the manufacture of high-strength materials from metallic polycrystalline filamentary material, e.g. iron, which has been deposited from the gaseous phase, wherein a mass of the filaments is consolidated by deposition of a metal thereon to join and bond the filaments at their points of intersection, whereafter the mass is briefly heated under pressure to produce a diffusion bond between the metal of the filaments and the metal deposited thereon and to compact the mass. Thereafter the mass may be impregnated with a metal of lower melting point. Loose unbonded masses of filaments may be similarly impregnated, particularly if the filaments are given a prior surface treatment to reduce oxidation and so ensure wetting of the filaments by the impregnating metal. Where the impregnating metal forms an alloy with the metal of the filaments, the latter may be provided with one or more intermediate layers of a non-alloying substance.

2 Claims, No Drawings

METHOD OF MANUFACTURE OF MATERIALS FROM POLYCRYSTALLINE FILAMENTS

This is a continuation of application Ser. No. 31,022, filed Apr. 22, 1970, now abandoned.

The invention is concerned with the combination of polycrystalline metal filaments, which are also known as polycrystalline whiskers, by metallurgical measures. The term polycrystalline metal filaments is intended to mean such metal filaments as originate from the gaseous phase and which, in the original state, are composed of extremely small and in most cases submicroscopically fine crystals (see German Patent No. 1,224,934). Examples of such polycrystalline metal filaments are iron filaments with a granular size of between 70 and 90 A and a carbon content of between 0.8 and 1.6 percent. These iron filaments are of extraordinary hardness, of between 1,300 kp/sq.mm. MHV and 2,400 kp/sq.mm. MHV and have tensile strengths of up to 850 kp/sq.mm.

It is well known that in sintered-powder metallurgy, in addition to more or less spherical powder particles, it is also advantageous to sinter elongated powder particles, e.g. dendritic material, and it is likewise known to sinter that metallic filaments, preferably into porous bodies. For the sintering of metallic filaments, the designation filament metallurgy was even introduced, although the sintering of fibrous materials has hitherto, in procedure, hardly differed from the sintering of powdered material.

These conventional metallic filaments (see Friedrich Eisenkolb, Fortschritte der Pulver-Metallurgie, 1963, Vol. 2, p. 904) do not however form part of the object of the invention, since in their strength properties and structure they do not differ from the conventinal basic materials of sintered powder metallurgy. The filaments obtained by drawing, spinning or cutting, as used in the so-called filament metallurgy, offer no substantial advantages over powders in terms of mechanical strength. They are significant rather more from the point of view of their applications.

In contrast, the present invention uses for the manufacture of high-strength materials polycrystalline filaments which are produced from the gaseous phase, in other words not produced from originally compact material. These filaments grow by aggregation of originally free metal atoms into their filament form and, by reason of unusual structure and an extremely high number of dislocations, they have outstanding strength which exceeds that of conventional metal filaments by more than a power of ten. It is true that, in addition to the polycrystalline filaments of the afore-described type, other high-strength filaments are also known, namely the so-called single crystal whiskers, appositely also referred to as hair crystals, but it is a known fact that these cannot be sintered because such a process destroys the cause of high strength, namely a virtually fault-free lattice structure.

The present invention arises from the relisation that the described polycrystalline filaments of high strength cannot be readily sintered by conventional processes and yield optimum results. Whereas the strength of sintered products from conventional powders and metal filaments generally depends on the degree of residual porosity and since the inherent strength of the starting material is not greatly affected by the sintering process, the results of the sintered powder metallurgical processing of polycrystalline filaments and the mechanical

properties of the materials thereby obtained depends to a great extent upon the duration of the sintering process, in fact to the opposite extent than with the sintering of conventional basic materials. It is well known that the strength of a sintered product generally increases with the duration of the sintering process, inter alia, while the sintering of polycrystalline filaments can, for equally long sintering times result in a diminution in the strength of the starting material and hence also of the sintered product.

The object of the invention is therefore to retain the valuable strength properties of the polycrystalline filaments during processing to form porous or compact materials. According to the invention, the filaments are first shaken, riddled or compressed to the desired pore volume, then are metallically bonded to one another at their points of intersection or contact and finally the thus consolidated porous mass is briefly heated to such a temperature that a diffusion exhange of atoms occurs between the metallic bonding substance and the filaments. Preferably the consolidation porous mass is compressed ruring the brief period of heating. The metallic bonding may be effected by passing a stream of carrier gas, charged with a thermally decomposable metal compound in vapour, mist or aerosol-like form, through the porous mass of filaments, the porous mass being maintained at the decomposition temperature of the relevant metal compound. The term decomposition temperature is in this case not the temperature of complete thermal decomposition but a temperature at which preferably a maximum of only some three-quarters of the weight of metal compound is decomposed.

The deposition of metals on the fibres gives rise to a metallic bonding or joining of the points of intersection of the filaments. In this state, the mass of filaments already has a considerable mechanical strength. The subsequent exposure of the metallised porous skeleton to an elevated temperature causes at least one type of atom, either that of the filaments or of the metallic deposition product, to penetrate the boundary layer between the filament surface and the metal deposit by the onset of diffusion. By virtue of the extremely finely crystalline metal deposition which is obtained from thermally decomposable metal compounds, which results in a maximum possible approximation of the metal deposit to the natural surface structure of the metal filaments, a spontaneous sintering or fusion on the aforesaid boundary interface occurs. The importance of the process described arises from the fact that with the unusually high hardness of the polycrystalline metal filaments, an approximation to this result is not possible by pressing and moulding of the filaments. The brief heating of the filaments which have been metallically prebonded, according to the invention, can be effected in a few seconds by per se known means, e.g. by induction heating, direct resistance heating, hot compression, etc.

EXAMPLE

Polycrystalline iron filaments with a carbon content of 1.3% C and a microhardness of 1,350 kg/sq.mm. MHV are shaken in a tube consisting of heat resistant non-conductive material, for example Al_2O_3,by means of a vibrator and two gas permeable carbon electrodes are applied one to each side of the shaken mass of filaments. After the mass of filaments has been de-aerated by passing a stream of argon through the gas permeable carbon electrodes, an electric current is fed to it through the electrodes which brings the porous mass of filaments to a temperature of for example 140°C by resistance heating, whereupon iron pentacarbonyl vapour is added to the stream of argon. This results in iron being deposited on the polycrystalline iron fialments, bonding the iron filaments into a mechanically rigid skeleton in the manner described. Thereafter, while pure argon is passed through it, this solidified filament skeleton is for a period of a few seconds brought to a temperature of 650°C by resistance heating in the same manner as previously but at increased current intensity, and at the same time a strong pressure is exerted from both sides on the heated filament skeleton by the two electrodes, the pressure being between 0.3 and 14 kg/sq.mm. according to the degree of residual porosity required. The bonding of the iron filaments using the procedure outlined in the present example can be achieved in the same way by thermal decomposition of nickel tetracarbonyl, molybdenum hexacarbonyl, tungsten carbonyl, dicomenchromium, dibenzolchromium, etc.

In an alternative method of carrying out the invention, the metallic bonding of the metal filaments is achieved by electro-less deposition of metals, in that one of the known reaction solutions for electro-less deposition, for example a solution for the electro-less deposition of nickel, is passed through the porous mass of filaments at the prescribed working temperature of for example 96°C until such time as a sufficient quantity of metal is deposited on the filaments, which is necessary for bonding at their points of intersection. Subsequently, the procedure is as previously described.

The advantage of using electro-less metal deposition for bonding the points of intersection of the filaments resides on the one hand in that metals can be used, the thermally decomposable metal compunds of which are too expensive and therefore uneconomical, and on the other in that the amorphous form in which metals are deposited by the electro-less process permits of a particularly marked approximation of the metal precipitate to the natural surface texture of the metal filaments to that the rapid onset of sintering or fusion of both types of metals at their boundary interface is encouraged. Furthermore, this process is additionally assisted by the known presence of phosphorus as a consequence of the deposition reaction. Finally, the onset of the diffusion bonding is also promoted in that the phosphorus present reduces the melting temperature of the metal deposit, which is directly connected with a more rapid diffusion.

A porous body made from iron filaments, produced and solidified in this way, can in known manner be impregnated with metals and metal alloys which have a lower melting point than the polycrystalline metal filaments and the metallic bonding substance, an essential condition being that the iron filaments are wetted by the impregnation metal. For this reason, it is advantageous to avoid oxidation on the overall surface of the already solidified metal filament skeleton, for which purpose this latter, after removal of the electrodes, is brought into contact under protective gas, with the appropriate metal melt, which by capillary action fills in the pores in the system. Naturally, synthetic plastics material can be used as the impregnation material by proceeding accordingly.

Although in theory and in practice, impregnation of a filament skeleton solidified in the manner described results in maximum possible solidification under the conditions indicated, it is of course also possible advantageously to apply the known impregnation process for porous sintered bodies to filament skeletons made from non-solidified polycrystalline metal filaments. The object of the invention, to manufacture high-rigidity materials from polycrystalline filaments, cannot however be readily achieved without using the above-described process for the primary metallic bonding of the point of intersection of the filaments, i.e. when utilising loosely shaken or riddled or pressed filaments, since the polycrystalline filaments have naturally a coating of oxide, however thin, without which, by virtue of their extremely large surface area, they would spontaneously oxidise, developing a considerable heat. Certainly it is obvious to remove the existing oxide coating by reductive measures prior to impregnation with metals, but the relatively high reduction temperature, for example in the case of reduction with carbon monoxide or hydrogen, will reduce the strength of the metal filaments in an undesirable degree.

Therefore, the invention resolves the problem of a direct impregnation of loose polycrystalline metal filaments in that these metal filaments already undergo a surface treatment while they are being manufactured, this surface treatment largely preventing a subsequent harmful oxidation, in any event sufficiently not to interfere adversely with the wetting stage of the impregnation process. The polycrystalline whiskers are, according to one embodiment of the invention, coated during their manufacture with a thin and only slowly oxidising metal coating to a thickness of 0.3 to 1 μm. for example with a coating of nickel, after which they never lose their wettability, even when stored. According to a further embodiment of the invention, the polycrystalline filaments which, when they are manufactured, initially have a metallically clean surface, are wetted with a liquid film, to the exclusion of air, safeguarding them against spontaneous oxidation until the impregnation process takes place, although the liquid used must be one which can be removed immediately prior to or during the impregnation process by complete evaporation. As examples of such liquids, paraffins or so-called vapour phase inhibitors such as dicyclohexyl-aminonitrite or 1-nitronaphthalene have proved successful.

These measures achieve the object of the invention, to combine polycrystalline filaments metallically into a compact material of high strength, avoiding a conventional sintering process and without having to allow for the strength of the filaments diminishing by excessively long processing temperatures, because the capillary wetting of the filaments with liquid metals occurs so rapidly that physical reactions which cause the loss of strength at elevated temperatures or when the filaments dwell for long periods in these temperatures, cannot arise to a dangerous extent.

The measures described, which are suitable for producing high strength bodies by metallic combination of polycrystalline filaments, do not however produce a complete success if these filaments are solidified by impregnation with metals which have a readiness to alloy with the material of these filaments. Such a case occurs for example if it is intended to combine iron filaments with light metal or light metal alloys. In this case, there is a danger that the iron filaments, while forming an alloy, may become more or less rapidly consumed by the impregnation metal. The invention resolves this industrially very important problem by manufacturing the polycrystalline metal filaments so that in the course of their thickness growth, one or more intermediate layers are incorporated which are not capable of alloying with aluminium and its alloys, or at least are only so capable with more difficulty than the basic metal of the polycrystalline metal filament. For example, according to one embodiment of the invention, polycrystalline iron filaments are produced so that their natural growth is interrupted on one or more occasions by an oxidation process or by the deposition of another metal such as tungsten or molybdenum or by the deposition of some other metal and subsequent oxidation of this metal. Metal filaments produced from iron in this way have in cross-section, where a plurality of the described intermediate layers are present, a structure similar to an onion skin, the surface of the filaments consisting of iron.

The object of avoiding the consumption of the polycrystalline fibres which come in contact with a molten batch of aluminum and its alloys during the impregnation process is thus achieved because although the outermost surface of the filaments can be consumed as an alloy is formed, the underlying coating of oxide or foreign metal represents an alloy-retarding barrier and all subsequent intermediate coatings of a foreign substance take on this same task one after another. The advantages of this embodiment of the invention include the fact that polycrystalline metal filaments with such a structure are suitable both for impregnation of a loose filament association as well as for the impregnation of a metal filament skeleton, in which filaments have been primarily metallically bonded at the points of intersection. In the latter case, it is expedient to establish the bonding of the points of intersection of the metal filaments by metal deposition, incorporating intermediate layers of foreign substances, as has just been described in the case of the manufacture of polycrystalline metal filaments.

The metallic impregnation of a mechanically rigid skeleton of bonded non-metal fibers according to the invention has as far as procedural technique is concerned, the decisive advantage that metallisation renders the non-metal filaments wettable while on the other hand the metallic bonding of the non-metallic filaments at the points of intersection, in the same way as with the pure metal filaments, enables the filament association to withstand the intense mechanical loading forces due to capillary forces without destruction. Even an intentionally intimate packing of the filaments in such a skeleton can therefore be maintained during the impregnation process, while is is known to be extremely difficult to achieve a high proportion of fibers solely by stirring loose fibers or filaments into a metal melt.

An example of this is the incorporation of Al_2O_3 filaments, high-rigidity carbon filaments, boron filaments, silicon whiskers and the like into a copper matrix.

I claim:

1. A process for the manufacture of high-strength materials from polycrystalline iron metal whiskers and filaments comprising:

providing a mass of iron whiskers which are grown by aggregation of the iron atoms into filament form;

pressing said whiskers into a compressed mass of the form or shape in order to provide a formed filament skeleton mass for later metal impregnation;

mechanically bonding iron metal to filaments in said skeleton filament mass to thereby connect filaments to each other at contact points by a step of depositing metal thereon;

said aforementioned metal depositing step being carried out by thermally decomposing iron pentacarbonyl metal compound in the vapor state to form decomposed iron metal which adheres mechanically to the skeleton of iron filaments and is next to the same type of atoms for diffusing;

thereafter heating and compressing said mass under a pressure between about 0.3 and 14 kg/sq mm, said heating being to a temperature of about 650°C by means of resistance heating for a period of about a few seconds which causes a diffusion exhange of atoms between the deposited metal and the filaments;

and impregnating the aforesaid heated product with a metal or metal alloy of lower melting point to thereby provide an impregnated mass of high-strength.

2. A process for the manufacture of high-strength materials from polycrystalline iron metal whiskers and filaments comprising:

providing a mass of iron whiskers which are grown by aggregation of the iron atoms into filament form resulting from iron pentacarbonyl decomposition;

pressing the mass of whiskers into a compressed skeletal mass of the form or shape in order to provide a formed filament skeleton mass for subsequent metal impregnation;

mechanically bonding nickel metal to said filaments in the compressed mass to connect to each other at contact points by a step of depositing metal thereon;

said aforementioned metal depositing step being carried out by depositing nickel to a coating thickness of from 0.3 to 1 millimicrons from a solution used for the electroless deposition of nickel under conditions of elevated temperature of about 96°C for a time which is sufficient in order to provide said metal thickness;

thereafter compressing said mass under a pressure between about 0.3 and 14 kg sq/mm while heating to a temperature of about 650°C by resistance heating for a period of about a few seconds and thereby causing a diffusion exchange of atoms between the deposited nickel metal and the iron filaments;

and impregnating the aforesaid heating product with a metal or metal alloy of lower melting point to provide an impregnated mass of high strength.

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