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TUNGSTEN BORIDE-CONTAINING ARTICLES AND PRODUCTION THEREOF

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ABSTRACT OF THE DISCLOSURE

Articles, preferably of filamentary form, containing or consisting essentially of tungsten boride have improved mechanical properties when the tungsten boride W_2B_5 constitutes at least 80% of the tungsten boride content. When the article consists of a tungsten boride core with an outer layer of boron, the latter is preferably amorphous.

The present invention is concerned with articles containing or consisting essentially of tungsten boride and with processes for their preparation.

It is known to manufacture complex materials by depositing boron on a suitably chosen metallic core. The deposition of the boron is effected by decomposing a gaseous mixture containing a boron halide on the metallic core while the latter is heated to an elevated temperature. When the metallic core is formed of tungsten, it is known that under the conditions used to effect the deposition of the boron, a number of compounds, all of which are tungsten borides, are formed by reaction between the boron and the tungsten. The formulae W_2B, WB, WB_2, W_2B_5 and WB_4 can be ascribed to these tungsten borides. We have now found that among the tungsten borides, the tungsten boride W_2B_5 possesses a remarkable combination of properties which make it, both by itself and when incorporated in complex materials, the product of choice.

According to the present invention, therefore, we provide articles containing or consisting essentially of one or more tungsten borides in which the tungsten boride W_2B_5 constitutes at least 80% of the tungsten boride content.

We have also found that among the tungsten borides other than W_2B_5, tungsten tetraboride WB_4 has, as compared with W_2B_5, the least valuable properties and that it is desirable to restrict the WB_4 content of such articles containing or consisting essentially of one or more tungsten borides.

The present invention also comprises, therefore, articles containing or consisting essentially of one or more tungsten borides in which the tungsten boride W_2B_5 constitutes at least 80% of the tungsten boride content and tungsten tetraboride WB_4 constitutes less than 15% of the tungsten boride content.

As stated above, complex materials containing tungsten borides are usually prepared by depositing boron on a suitably heated tungsten core. As the boron is deposited on the tungsten, tungsten borides are formed leading to conversion of all or part of the tungsten and of all or part of the boron which is deposited. When the boron deposit is rather thick, a composite material is obtained comprising a core of tungsten boride which can, in the appropriate circumstances, still contain an inner

core of unconverted tungsten, and an outer layer of boron. However the mechanical properties of such a composite material are better when all the tungsten is converted into tungsten boride.

According to a preferred feature of the invention, therefore, the articles according to the invention do not contain any unconverted tungsten.

The outer layer of boron which may be present in the articles according to the invention, preferably consists of amorphous boron. The term "amorphous" used in this specification does not imply that the boron atoms are in a non-crystalline state and entriely disorganised, but that the boron crystallites are sufficiently small for the material to appear to be amorphous when examined by X-rays. We have found that the best mechanical properties are present in materials in which the boron crystallites are as small as possible; it is preferred, in fact, that the crystallites should have a mean size of about 60 A.

The articles according to the invention are prepared by suitably controlling the conditions under which the deposition of the boron on a core of tungsten is effected. Filamentary or threadlike articles are preferably prepared. The deposition of boron arises from the thermal decomposition and the chemical reaction of a boron halide, such as boron trichloride, mixed with hydrogen. The process is carried out, for example, on a 12.7 micron tungsten filament which is electrically heated by Joule effect, the ends of the filament being subject to a potential difference sufficient to heat the filament to a temperature such that amorphous boron having crystallites of well defined dimensions, is obtained.

The parameters of the process are as follows: (a) total gaseous mass supply, (b) mass fraction of the reactants, (c) temperature of the filament, (d) speed of transport of the filament, (e) diameter of the reactor, (f) length of the reactor, (g) sequence of the reactors, and (h) running system chosen.

The choice of the values of these parameters influences both the nature of the boron deposited and the interaction of the boron and the core. These two effects influence in turn the tensile strength and the homogeneity (in terms of the variation of the strength values around the mean value) of the filamentary product obtained.

The control of the overall tungsten boride content and of the proportion of W_2B_5 and WB_4 in the overall tungsten boride content, in the filamentary material obtained, is effected by precisely regulating the temperature and the time for which the filament is heated to a high temperature in order to effect boron deposition. Thus if the starting material is a tungsten filament 12.7 microns in diameter, complete conversion of the tungsten into tungsten borides, of which at least 80% is W_2B_5, is obtained by heating the filament in the presence of the gaseous mixture whose decomposition leads to boron deposition, to a temperature of from 1050 to 1150° C. for a period of about 1 minute. We have ascertained that the best mechanical properties are obtained when all the tungsten of the material is converted into tungsten borides by the time the material leaves the first reactor. In the case of the starting material mentioned (i.e. a filament having a diameter of 12.7 microns) this result is obtained by heating within the specified temperature range (1050–1150° C.) for a period of at least 12 seconds.

It will be apparent that if the diameter of the tungsten filament is larger, the time of heating within the specified temperature range should be longer. As regards obtaining the deposition of amorphous boron having crystallites of very small dimensions, the following observation has been made:

When the boron deposit changes from the "amorphous" state previously defined to the crystalline state, it produces

a detectable electrical instability in the heating of the substrate by Joule effect. Thus whatever may be the cause of this allotropic variant of the boron arising, that is to say whatever may be the parameter of deposit production, the variation of which causes the change in the structure of the deposit, the operative can use the detection of such electrical instability to prevent this allotropic variation.

We have found that in order to obtain boron deposits having the best mechanical characteristics conditions should be used leading to the formation of an amorphous boron, more particularly conditions as close as possible to, but not the same as, those in which the commencement of the allotropic conversion of amorphous boron to crystalline boron is detectable by the above-mentioned electrical instability.

When all the previously described production parameters are constant, this allotropic conversion takes place at a particular fixed electrical intensity and, therefore, at a particular temperature.

For a given reactor and given operating parameters, the electrical intensity used is suitably fixed at 3% below the experimentally determined value at which the instability phenomenon occurs with the same reactor and operating parameters. The electrical intensity is preferably regulated by means of an apparatus capable of maintaining the chosen value to within better than 1%.

We claim:

1. A process for the production of an article containing at least one tungsten boride, which comprises the step of heating an article consisting of a core of tungsten having around said core a layer of boron to a temperature of from about 1050 to about 1150° C. under conditions as close as possible to, but not the same as those indicated by electrical instability in the heating of the tungsten, which cause the structure of the deposited boron to change from amorphous to crystalline for a time sufficient to convert at least a part of the tungsten to tungsten boride wherein at least 80% of said tungsten boride is tungsten pentaboride and less than 15% of said tungsten boride is tungsten tetraboride.

2. The article produced according to the process of claim 1.

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