United States Patent Office 3,823,029 Patented July 9, 1974

3,823,029

METHOD FOR COATING GRAPHITE FILAMENTS WITH REFRACTORY METAL CARBIDES

Moinuddin S. Rashid, Ames, Iowa, assignor to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed Aug. 1, 1972, Ser. No. 276,989
Int. Cl. B44d 5/12
U.S. Cl. 117—118 6 Claims

ABSTRACT OF THE DISCLOSURE

Fine graphite filaments for use as reinforcements in metals and alloys are coated with a thin layer of a refractory metal carbide by heating the filaments in a low-melting metal containing a small amount of a refractory metal.

CONTRACTUAL ORIGIN OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

This invention relates to a method for coating fine graphite filaments. More specifically, this invention relates to a method for coating fine graphite filaments with a refractory metal carbide.

The reinforcement of metals and alloys with filaments having qualities of low density, high strength and high modulus promises a new class of advanced engineering materials. Presently available filaments can be divided into several groups, such as amorphous, single crystal, multiphase and polycrystalline. Each filament type has its advantages and limitations and the selection of a given filament for a given metal-matrix composite is based partially on the conditions imposed by the application.

Graphite filaments, which are polycrystalline, appear to be promising for strengthening metals for use at elevated temperatures. The average strengths of commercially available graphite filaments range as high as 400,000 p.s.i., although experimental grades of graphite have been reported to have tensile strengths of 500,000 p.s.i.

Besides their superior strength at room temperature, graphite filaments have the ability to withstand extremely high temperatures in a protective atmosphere without loss of stiffness or strength. This property makes graphite filaments far superior to most filaments as reinforcements in composite materials for use at elevated temperatures. Also, graphite filaments have a small diameter of about 8 to 10μ, which makes it possible to fabricate them using glass-fiber technology, and a low density, which ensures that the strength/density and modulus/density ratios will be high.

Although the outlook for graphite is promising, the material has one major drawback which has limited its use in metal-matrix composites. It has a very high reactivity with most metals at elevated temperatures. This shortcoming must be eliminated or reduced before graphite will be suitable for use as a reinforcing filament. One possible solution is to develop a suitable protective coating which will prevent direct contact between the filament and matrix.

Theoretically, the coating can be formed by deposition of the metal on the surface of the filaments and interdiffusion with the graphite at elevated temperatures. However, most established processes cannot be used successfully with filaments because of the stringent conditions which are imposed by their small size and the required high quality of the coating. To ensure against failure, the

coating must be very adherent, continuous and of a uniform thickness. Also, it must not be more than a few microns thick. A thick layer of carbide could be a source of weakness in the composite material and, since presently available graphite filaments are only 8μ or less in diameter, the formation of a thick carbide coating will lead to a considerable reduction in the diameter of the filament.

SUMMARY OF THE INVENTION

A method has been developed for forming thin refractory metal coatings on graphite filaments having the desired properties enumerated above. In accordance with this invention, the fine graphite filaments can be coated with a refractory metal carbide by contacting the filaments with a low-melting-point metal containing ½ to 5 weight percent (w/o) of a refractory metal to form a charge, heating the charge to a temperature of about 1400° C. in an inert atmosphere for a short period of time, whereby a coating of a refractory metal carbide is formed on the surface of the filaments, cooling the charge and separating the coated filaments from the low-melting-point metal-refractory metal alloy.

It is one object of this invention to provide fine graphite filaments suitable for reinforcing metal composites.

It is another object of this invention to provide fine graphite filaments suitable for reinforcing metals in a high-temperature environment.

It is another object of this invention to provide fine graphite filaments having a refractory metal carbide coating.

It is another object of this invention to provide a method for coating graphite filaments with a refractory metal carbide.

It is still another object of this invention to provide a method for coating graphite filaments with a refractory metal carbide for use in the reinforcement of metals and alloys.

It is a further object of this invention to provide a method for coating garphite filaments with a refractory metal carbide which is even, continuous and of uniform thickness.

Finally, it is the object of this invention to provide a method for coating graphite filaments with a refractory metal carbide by heating the filaments in the presence of a low-melting-point metal containing a refractory metal.

DESCRIPTION OF THE PREFERRED EMBODIMENT

These and other objects may be met by contacting the graphite filaments to be coated with a low-melting-point metal such as tin containing about 1 w/o of a refractory metal such as niobium or tantalum to prepare a charge, heating the charge in an inert atmosphere to a temperature of about 1400° C., maintaining the charge at this temperature for 2 to 3 minutes, until the refractory metal coating is formed, cooling the charge and separating the coated filaments from the metal.

Although tin is the preferred low-melting-point metal, other low-melting-point metals such as bismuth and lead are also satisfactory.

Although niobium and tantalum are the preferred refractory metals for the process of this invention, other metals such as molybdenum, zirconium, titanium and hafnium should also provide a satisfactory refractory metal coating on the fine graphite filaments.

The concentration of refractory metal present in the low-melting-point metal may range from about ½ to 5 w/o, although ½ to 1½ w/o is preferred and about 1 w/o is most preferred. Higher concentrations may result in a complete reaction between the refractory metal and the graphite filament, thus completely consuming the graphite. The lower concentration permits improved con-

trol over the depth of the carbide coating on the graphite filament. The ratio between the amount of refractory metal and the graphite filaments is not critical as long as there is sufficient refractory metal present to react with the graphite to form the metal carbide.

Heating should take place under an inert gas such as helium or argon to prevent any undesirable reactions from taking place between the graphite or refractory metal and the atmosphere.

Since the process of this invention is diffusion controlled, the thickness of the coating is controlled by carefully varying the time and temperature conditions. In general, it is believed that a 2μ thick coating on the fine graphite filaments will provide a sufficient diffusion barrier to protect the remaining graphite filament, and the conditions given herein are directed toward providing a coating of approximately this thickness; however, it is obvious that, by varying certain parameters of this method thicker coatings can be applied should they be necessary.

The temperature to which the charge is to be heated will depend upon the melting temperature of the low-melting-point metal and the amount of refractory metal which it contains. In general, it was found that a temperature of 1350 to 1450° C. was satisfactory for the compositions described herein, while a temperature of 1400° C. is preferred.

The length of time the charge remains at these temperatures is also critical to control the depth of the refractory metal carbide coating. In general, it was found that by maintaining the temperature at about 1400° C. for 2 to 3 minutes before permitting the container to cool to room temperature was sufficient to obtain about a 2μ coating of refractory metal carbide. In order to control the length of time the charge was at the diffusion temperature, the charged crucible was heated rapidly (less than 10 minutes) to 1400° C.

Any crucible is satisfactory to practice the method of this invention which will not react with the constituents. In general, a graphite crucible was found to be satisfactory, although it is necessary to prepare a refractory metal carbide coating on the inner surface of the crucible to prevent loss of the small amount of the refractory metal present by reaction with the crucible. This coating can be readily applied by filling the crucible with low-melting-point metal containing several weight percent of refractory metal and heating the filled crucible under an inert atmosphere to at least about 1400° C. for a period of time sufficient to react the refractory carbide with the inner surface of the graphite to form a refractory metal carbide coating on the inner surface of the crucible.

The refractory-metal-carbide-coated graphite filaments may be separated from the low-melting-point metal by methods known to those skilled in the art. For example, the low-melting-point metal could be dissolved in a concentrated mineral acid or the charge could be heated in a vacuum to a temperature sufficiently high to evaporate the alloy, thus leaving the refractory-metal-carbide-coated graphite filaments.

EXAMPLE I

Twenty-mesh tin powder and ½-inch-long segments of fine graphite filaments were stacked in alternate layers inside a graphite crucible which had previously been coated with niobium carbide to prevent a depletion of the refractory metal by the walls of the crucible. All filaments in the crucible were placed along the same axis. Approximately 1 w/o −325 mesh niobium powder was sprinkled on top of the tin and gradually worked into the crevices by vibrating the crucible, thereby forming the charge. The charged crucible was heated to about 1400° C. under a helium atmosphere at a fast rate (less than 10 minutes) in a carbon resistor furnace and held at that temperature for 2 to 3 minutes before cooling the charge to room temperature.

Electron-probe scans made on polished sections across the graphite/carbide and carbide/tin interfaces indicated that the niobium was concentrated in the carbide coating and in a thin layer (reaction zone) adjacent to the carbide/tin interface.

The metallographic examination also showed that the thickness of the coating was uniform and that no cracks were present except when there was a large pore in the graphite. These properties remained unchanged when the coating of Nb_2C was converted to NbC. Both Nb_2C and NbC were extremely adherent to the graphite and did not chip off when the coated surface of the specimen was ground on a 600-mesh SiC polished wheel.

The metallographically polished specimens were also used in the electron-probe microanalysis. Line scans for niobium were made across the diameter of several filaments and it was determined that no measurable amount of niobium had diffused into the graphite filament and that the niobium present was located in the carbide coating.

EXAMPLE II

Tin powder and ½-inch-long segments of graphite filament were stacked in alternate layers inside a graphite crucible which had previously been coated with a tantalum carbide coating. Approximately 1 w/o −325 mesh tantalum powder was sprinkled on top of the tin and gradually worked into the crevices by vibrating the crucible, thereby forming the charge. The charged crucible was heated to about 1400° C. under a helium atmosphere at a fast rate (less than 10 minutes) in a carbon resistor furnace and held at that temperature for 2 to 3 minutes before cooling the charge to room temperature.

The coated filaments were examined as described in Example I and were found to have a uniform, continuous coating of tantalum carbide.

EXAMPLE III

Five different commercially available graphite filaments were coated with niobium and tantalum carbide by the method described in Examples I and II. They were:

A. Polyacrylonitrile-derived (PAN):

1. Hercules Inc., HM–S, high-modulus
2. Hercules, Inc., HT–S, high-strength
3. Morganite, Type I, untreated, high-modulus, polyacrylonitrile
4. Morganite, Type II, untreated, high-strength

B. "Rayon" type:

1. Thornel-50, PVA sizes 2 ply yarn

The coated filaments were then examined as described in Example I. The coating on the "Pan" type filaments which have a circular cross section and a smooth surface was of a superior quality. It was continuous and uniform on more than 95% of the filaments. There were very few filaments which were either partially or irregularly coated. Also, the coating on all the filaments in an ingot had an almost identical thickness of approximately 2μ.

The quality of the coatings on the "Rayon" type filaments does not appear to be regular as was the coating on the "Pan" type of filaments and this is basically due to the difference in the surfaces of the two types of filament. The crenulated edges on the "Rayon" type filaments cause the graphite/carbon interface to be irregular. As the interface advances, the reduction in the size of the filaments as well as the surface of the coating become crenulated. Although these coatings were crenulated, they were still very continuous and the average coating thickness on most of the filaments in an ingot was uniform. However, due to their smaller size, a few of the filaments were completely converted to carbide. The irregular nature of the coating has one additional disadvantage. It could cause the effect of notches on the surface which could lead to the degradation of the tensile strength of the filament.

As can be seen from the examples, the method of this invention will successfully produce an even, uniform re-

fractory metal carbide coating on most available types of fine graphite filaments.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of forming a thin refractory metal carbide coating on graphite filaments comprising: contacting the filaments with a low-melting-point containing ½ to 5 weight percent of a refractory metal to form a charge, said low-melting-point metal being selected from the group consisting of tin, bismuth and lead, and said refractory metal being selected from the group consisting of niobium, tantalum, molybdenum, zirconium, titanium and hafnium; heating the charge to a temperature of about 1350–1450° C. under an inert atmosphere and maintaining this temperature for 2 to 3 minutes whereby a thin coating of refractory metal carbide is formed on the filaments; cooling the charge and separating the coated filaments from the low-melting-point metal and refractory metal.

2. The method of claim 1 wherein the low-melting-point metal contains about 1 weight percent of a refractory metal and the charge is heated to 1400° C.

3. The method of claim 2 wherein the low-melting-point metal is tin and the refractory metal is niobium.

4. The method of claim 2 wherein the low-melting-point metal is tin and the refractory metal is tantalum.

5. A method of forming a thin refractory metal carbide coating on graphite filaments comprising: packing the filaments into a graphite crucible, adding to the crucible and filaments a mixture of powdered tin containing about 1 weight percent of a powdered refractory metal selected from the group consisting of niobium and tantalum to form a charge; heating the charge within a period of 10 minutes to about 1400° C. under an inert atmosphere and maintaining this temperature for 2 to 3 minutes whereby a thin coating of refractory metal carbide is formed on the 9 filaments; cooling the charge and separating the coated filaments from the tin and refractory metal.

6. The method of claim 5 comprising the additional step of forming a metal carbide coating on the graphite crucible before preparing the charge to prevent depletion of the refractory metal in the charge.

References Cited

UNITED STATES PATENTS

2,929,741	3/1960	Steinberg	29—195 A X
3,366,464	1/1968	Guichet et al.	117—21 X
3,369,920	2/1968	Bourdeau et al.	117—121 X

WILLIAM D. MARTIN, Primary Examiner

T. G. DAVIS, Assistant Examiner

U.S. Cl. X.R.

117—119, 160, 169 R