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F. S. SCHULTZ ET AL
COATED MOLYBDENUM ARTICLE

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Fig 1

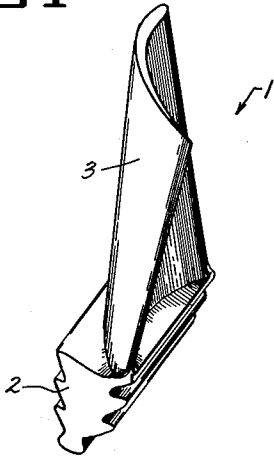


Fig 2

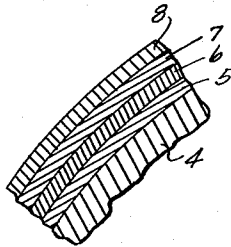


Fig 3

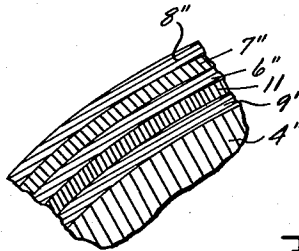
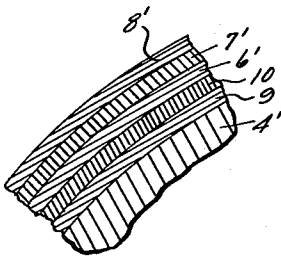


Fig 4

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COATED MOLYBDENUM ARTICLE

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This invention relates to protective surfaces for structural components operating at elevated temperatures and, more particularly, to protective surfaces for molybdenum and molybdenum base alloys which have both oxidation resistance and high resistance to impact, abrasion, and erosion.

Molybdenum possesses certain desirable physical characteristics which make it adaptable for structural components exposed to high temperatures. It has been found that the physical properties of molybdenum at elevated temperatures make it a most useful metal for various gas turbine applications such as buckets, blades, valves, nozzles and the like. Unfortunately, however, molybdenum and its alloys oxidize very rapidly above 1400° F. Temperatures in the range of 1400° F. and above are quite common in gas turbine applications. In order to use molybdenum or its alloys in such high operating temperatures, it is desirable to coat the surface of the molybdenum with an oxidation resistant material.

Heretofore, various types of coatings have been found which will protect the molybdenum article from oxidation at elevated temperatures under static conditions where the coated article is subjected to little, if any, external forces from a flow of gases. Such coatings have been found to be satisfactory when used in applications where the coated molybdenum article is in a static atmosphere. However, the same coatings which are found to be satisfactory under static conditions are found to be unsatisfactory when used in certain gas turbine applications. Articles having the aforementioned types of coating are installed in a gas turbine operating substantially above 1400° F. It is found that the severe operating conditions encountered by the article because of high gas velocities and the entrainment of particles in the gases cause failure in certain portions of the oxidation resistant coating. It has been found that these failures are due to the effects of impact, abrasion, and erosion of the particles entrained in the hot gases. These localized failures of the oxidation resistant coating result in oxidation and ultimate destruction of the molybdenum or molybdenum alloy article. It has been found that even a very small failure in the coating is very serious since the slightest exposure of the molybdenum or molybdenum alloy to the atmosphere will cause rapid oxidation of the exposed area. As oxidation progresses, an increasingly large area of the molybdenum or molybdenum alloy is exposed resulting in failure of the coated article.

One of the objects of this invention is to obviate the above difficulties.

Another object of this invention is to provide an oxidation resistant coating for a molybdenum article which has extremely high resistance to impact, abrasion, and erosion.

Briefly stated, in accordance with one aspect of our invention, we provide a molybdenum or a molybdenum alloy article having an oxidation resistant protective coating containing the element boron and having a coating of chromium superimposed over the coating having a boron content. The article is heat treated to form an intermetallic layer of chromium boride. The intermetallic layer, so formed, is highly oxidation resistant and is extremely hard so that the article has substantially increased resistance to impact, abrasion and erosion.

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The invention hereinafter described is applicable to any regularly or irregularly shaped molybdenum or molybdenum alloy object that is to be protected for operation at elevated temperatures. For purposes of illustration, however, the invention will be described in connection with the coating of a gas turbine bucket since this is a rather typical application for protective surfaces of the type disclosed by this invention. It is to be understood, however, that the protective surface as herein described is applicable to any molybdenum or molybdenum base alloy whether it is a flat sheet or an irregularly shaped object, the latter being illustrated by a turbine bucket as hereinafter set forth.

Our invention will be better understood from the following description taken in connection with the accompanying drawing and its scope will be pointed out in the appended claims.

In the drawing, FIGURE 1 is a perspective view of a turbine bucket; FIGURES 2, 3 and 4 are typical cross sections of a coated turbine bucket showing various methods of carrying out the invention wherein the thickness of the layers applied to the turbine bucket are greatly exaggerated for purposes of illustration.

Referring to the drawing, FIGURE 1 shows a typical turbine bucket. The turbine bucket is generally indicated at 1 comprising a base or root portion 2 and a blade portion 3. The blade portion 3 comprises a molybdenum or molybdenum alloy material which is to be protected for oxidation as well as impact, abrasion and erosion resistance. The first coating that may be applied is an oxidation resistant alloy containing boron. One method of applying a protective coating containing boron is set forth in detail below.

The first coating is oxidation resistant and may be applied by flame spraying. In carrying out this method the molybdenum or molybdenum alloy base represented in FIGURE 2 by the portion 4 which is a segment of the blade 3 shown in FIGURE 1 is first chemically cleaned. This may be done by electro-polishing until the base metal preferably obtains a brilliant metallic mirror-like finish although a highly reflective surface is not absolutely essential as will hereinafter be apparent. Various solutions, temperatures and times may be employed in the electro-polishing operation, the only limitation being that the base metal must be treated to avoid a "frosty" finish.

Having obtained a preferably mirror-like finish on the base metal, the surface is then roughened by grit-blasting. It is important that clean and dry grit be used in the grit-blasting operation. Good results were obtained by using a number 46 grit in preparing the turbine bucket used for illustration herein but it is to be understood that the size of the grit may vary over a wide range. It is merely essential that the base metal be grit-blasted sufficiently to form a roughened surface having a dull matte finish. The surface is sufficiently roughened to form a mechanical bond by an interlocking action between the first sprayed particles and the base metal. The dull matte finish described can be tested by holding the treated base metal to the light to see that there is a minimum of reflectivity. Following this operation the article is ready for application of the first coating.

Following the above preparation, an alloy containing boron is flame sprayed on the molybdenum base portion to obtain a first oxidation resistant coating. One type of coating material that may be used is a nickel base nickel-silicon-boron alloy which preferably should be of low carbon content. In addition, the particle size should be limited in order to obtain a dense coating which will have suitable oxidation resistance in itself. We have found in practice that such a nickel-silicon-boron alloy having

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particles no larger than -200 mesh and having a final as fused hardness no greater than 40 on the Rockwell C scale was satisfactory. In addition, it is desirable that the spraying take place in a reducing flame. The spraying apparatus may be of the conventional type for applying the coating to a desired thickness. It was found that a thickness of approximately .004-.005 inch is very satisfactory. The above procedure will produce a satisfactory coating on the molybdenum article which will in and of itself protect the article from oxidation at elevated temperatures.

After applying the coating, the bucket is heat treated in order to fuse the sprayed composition to the molybdenum or molybdenum alloy base metal 4. The heat treatment is preferably carried out in a reducing atmosphere such as a dry hydrogen atmosphere. The heat treatment process is best carried out in three steps, viz. preheating, fusing and cooling off. Preheating is carried out below the fusing temperature of the sprayed coating; for example, the range between 1500° F. and 1900° F. During such preheating, a partial sintering takes place between the particles of the sprayed coating. After preheating, the bucket is moved into the fusing or hot zone of the furnace. This zone is maintained at a temperature at or above the fusing temperature of the alloy being fused to the base metal. In the case of the sprayed coating herein discussed, the temperature in the fusing zone is approximately 2100° F. When the bucket is placed in the fusing zone, the sprayed coating melts, fuses, and forms a metallurgical bond between the coating and the base metal consisting of complex intermetallics. As shown in FIGURE 2, the metallurgical bond is shown at 5 and the sprayed alloy coating containing boron is shown by the layer 6. The fusing temperature used, which in this case is 2100° F., depends upon several characteristics of the process such as the type of reducing atmosphere, the dew point, the preheat time and temperature. The fusing temperature may vary for different coating alloys that meet the above mentioned requirements of the nickel-silicon-boron composition. After fusing, the bucket is cooled and this is preferably done in a reducing atmosphere although the reducing atmosphere is not absolutely essential.

In the case of an irregularly shaped object, such as a turbine bucket, it is necessary to rotate the bucket during fusing to prevent the sprayed coating from sagging and running while it is being brought up to fusing temperature in the fusing zone of the furnace. Rotation of the bucket during fusing also tends to result in a completely uniform coating thickness on the bucket. In the case of an article having a flat surface it may not be necessary to rotate the article.

By following the above process a uniform oxidation resistant coating is applied to the molybdenum or molybdenum alloy base metal which does possess excellent resistance to nominal impact, abrasion, erosion and thermal shock. It is to be understood, of course, that other methods and types of oxidation resistant coatings may be applied. A requirement of such a coating would be that it contains boron for reasons that will hereinafter become apparent. It may also be possible to apply this coating by other well known methods.

After applying the first coating which is inherently oxidation resistant, a second coating is superimposed over the first coating. The second applied coating is chromium which may be applied by any known process such as electro-plating.

The chromium coating may be applied by buffing the first coating 6 in order to remove the oxide film. After buffing, the bucket is cleaned by any well known chemical cleaner in order to assure a clean surface to which the chromium coating will adhere. After cleaning, the bucket is rinsed to insure that the cleaning agent has been removed. The bucket is next immersed in an acid activator in order to reactivate the nickel bearing sur-

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face of the first coating where the first coating is a nickel bearing alloy as used for illustration herein. The bucket is again rinsed and is then ready for chromium plating. The bucket is then chromium plated in a conventional chromium bath. Good results were obtained by using a current density of approximately 2 amperes per square inch and holding the bath temperature at 130-170° F. with an immersion time of approximately one hour. It is to be understood, of course, that other plating conditions may be used that will satisfactorily plate the chromium on the bucket. The thickness of the chrome plate is not critical but good results have been obtained by using a thickness of .001-.002 inch.

The bucket is next treated in order to form a hard intermetallic layer 7 between the chromium coating 8 and the boron containing alloy 6 as shown in FIGURE 2. During heat treatment some of the boron from the layer 6 containing boron reacts with the chromium in the layer 8 to form an intermetallic layer 7 of chromium boride. Chromium boride is very hard and very oxidation resistant. The heat treatment results in the formation of the very hard intermetallic layer 7 over the coating 6 containing boron. Simultaneously with the formation of the chromium boride intermetallic layer 7, it was found that the diffusion of the boron from the alloy layer 6 raised the melting point of the nickel-silicon-boron coating used for purposes of illustration herein. Experimentally it was found that the melting point of the nickel-silicon-boron layer was raised by at least some 200° F. The heat treatment is carried out at 1800° F. to 2100° F. and the time employed is a function of the temperature used. Good results were obtained experimentally by using a temperature of 2000° F. and a time of four hours.

By changing the time and temperature of heat treatment, the thickness of the intermetallic chromium boride layer 7 may be varied to obtain the most desirable thickness for a given application and set of operating conditions to be encountered. The heat treatment may be carried out in a hydrogen atmosphere although it is not essential to do so in order to obtain the necessary diffusion to form the intermetallic layer 7. The intermetallic layer 7 created by the above heat treating process has extremely high resistance to impact, abrasion and erosion. In fact, the resistance of the intermetallic layer 7 to impact, abrasion and erosion is substantially greater than would be the resistance of either of the coatings 6 or 8 when used alone or if combined without further heat treatment.

As noted previously, the fusion of the coating 6 containing boron produces an intermetallic layer 5 between the coating 6 and the base molybdenum 4. In some cases it may be desirable to provide an intermediate layer between the layer 6 containing boron and the molybdenum or molybdenum alloy base material 4. Such a system is shown in FIGURE 3, wherein the molybdenum base or body portion 4 has a layer of chromium 9 deposited thereon by any suitable process such as electro-plating, for example. The chromium layer 9 is then grit blasted in the same manner as the molybdenum or molybdenum base alloy 4 was prepared and then the coating 6 containing boron is sprayed on and fused. During the fusion process, an intermetallic layer 10 of chromium boride is formed between the chromium layer 9 and coating 6 containing boron. The chromium layer 8 is then deposited over coating 6 as previously described and subsequently heat treated to produce a second intermetallic layer 7 as outlined for the system shown in FIGURE 2. In the system of FIGURE 3, the chromium layer 9 prevents the formation of complex intermetallics at the molybdenum or molybdenum base alloy interface as the layer 5 of FIGURE 2, for example.

In still other types of service it may be desirable to retard formation of an intermetallic layer between the chromium layer 9 and the boron alloy 6 as at 10 in FIGURE 3. This may be done by using the system

shown by FIGURE 4. In the system of FIGURE 4 the base molybdenum or molybdenum alloy portion 4'' has a first layer of chromium 9' which may be applied by any suitable process such as electro-plating for example. A second layer 11 of nickel is applied over the first layer 9' of chromium by any satisfactory known process such as spraying, electro-plating or the carbonyl process. Following the application of the nickel layer 11 the part is heat treated in order to form a diffusion bond between the nickel layer 11 and the chromium layer 9' and the chromium layer 9' and molybdenum or molybdenum alloy base 4''. Good results were obtained by gradually warming the part to 1400° F., maintaining the temperature for one hour, then raising the temperature to 1600° F. for one hour and finally raising the temperature to 1800° F. for two hours. This heat treatment is carried out in a dry hydrogen atmosphere. The nickel layer 11 is then cleaned and grit blasted in preparation for the application of coating 6''. The outer layers 6'', 7'' and 8'' are then applied and formed in the same manner as previously described for the article shown in FIGURE 2.

As aforesaid, the reason for using the intermediate layers between the boron containing alloy coatings 6' and 6'' of the FIGURE 3 and 4 systems and the molybdenum of the base 4' and 4'' is to prevent the formation of complex intermetallics between the alloy containing boron and the molybdenum which may be detrimental in some applications. These intermediate layers may be necessary in order to give the coated article the properties required to resist the stresses and temperatures encountered in a given set of operating conditions. From a practical standpoint, of course, it is desirable to limit, as far as possible, the layers to the least number which will give satisfactory operating results in order to reduce processing time and costs. The criteria for establishing the number of intermediate layers, if any, which will give the best results under any set of operating circumstances must be determined by the operational use of the coated article.

While particular embodiments of the invention have been illustrated and described, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention and it is intended to cover in the appended claims all such

changes and modifications that come within the true spirit and scope of the invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. An impact and oxidation resistant article of a material selected from the group consisting of molybdenum and molybdenum base alloys and having a composite surface system metallurgically bonded together into said article, said composite surface system consisting of: a first coating of a nickel base, nickel-silicon-boron flame spraying alloy metallurgically bonded to said article; an intermetallic chromium boride second portion metallurgically bonded to said first coating; and a third coating of chromium metallurgically bonded to said second portion; said chromium boride portion being located between and being the product of interdiffusion of said first coating and said third coating.

2. A molybdenum alloy turbine bucket including a composite surface system metallurgically bonded together and to said turbine bucket, said surface system including an impact and oxidation resistant portion consisting of a flame sprayed first coating of a nickel base, nickel-silicon-boron flame spraying alloy; an intermetallic chromium boride second portion metallurgically bonded to said first coating; and an electrodeposited chromium third coating metallurgically bonded to said second portion; said chromium boride second portion being located between and being the product of interdiffusion of said first coating and said third coating.

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