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OXIDIZING PROCESS FOR FERROUS ALLOYS CONTAINING AT LEAST 5% CHROMIUM

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This invention relates, in its broadest aspects, to the high temperature ceramic coating of certain metals and particularly to methods of treating the surface of certain metals prior to and in preparation for coating with high temperature resistant ceramic. Specifically the invention contemplates a method of surface treating chromium steels, stainless steels, the so-called super alloys, and all like metal alloys having a minimum content of 5% chrome in order to adapt such surfaces for the subsequent application of ceramic coatings.

Ceramic coatings for the types of metals mentioned above, which are of comparatively recent origin, are characterized by excellent stability at temperatures exceeding 1700° F., good thermal shock resistance, and strong adherence. This latter property, however, is not necessarily an inherent characteristic of the coating itself but on the contrary usually stems from careful preparation of the surface of the basis metal prior to coating. It is well recognized in the art that, despite the general excellence of the coating, its adherence as well as other desirable properties related to and depending on good adherence, depends in great measure on the surface condition of the basis metal at the time the coating is applied. Because of this fact and its general recognition in the art, it has been standard practice heretofore to utilize a lengthy and costly combination of pickling and sand-blasting processes to obtain an etched or roughened surface on the metal to be coated, since it was believed that such a surface was essential to assure proper adherence of the ceramic. Consequently, all known prior art methods of coating high temperature ceramics on a metal base include a sand-blast step as a necessary preliminary procedure.

Despite its general acceptance and almost universal use, sand-blasting has a number of disadvantages which render it highly undesirable as a method of surface preparation particularly when dealing with thin metal and/or highly complex parts. It distorts parts and thins the metal excessively, often abrading a hole in the part, which must then be discarded. It is particularly unsatisfactory for the treatment of parts of complex form where some areas are practically inaccessible to the abrasive. Even where the aforementioned difficulties do not exist, the fact that even a simple sand-blast system is costly and cumbersome is an important disadvantage.

Nevertheless, these short-comings and disadvantages of prior processes have been tolerated for lack of any alternate process for providing a metal surface to which ceramic coatings could properly adhere.

The present invention contemplates a novel method of preparing metallic surfaces for the application of ceramic coatings which in its broader aspects involves the formation of a microscopically thin oxide film on the surfaces to be coated.

A number of methods have been proposed heretofore, for applying oxide films to metals. The type of oxides applied, the function and characteristics of these oxides, and the types of metals susceptible of treatment with

such prior art methods are manifold. Examples of such methods are given in U. S. Letters Patent No. 2,227,469 and No. 2,315,564. These oxide films, however, are not developed for the purpose of promoting adherence of high temperature ceramic coatings and are not satisfactory for such use primarily because, being deposited on the surface of the basis metal, their ability to adhere thereto is limited. According to the present invention, the exposed surfaces of metals are converted to an oxide which is an integral part of rather than a layer deposited on the metal surfaces.

It is therefore a primary object of the present invention to provide a novel method of surface preparation for metals which will insure superior bonding of ceramic coatings thereto.

Another object is to provide improved methods of preparing metal surfaces for ceramic coating, which are comparatively inexpensive, and far more rapid of accomplishment than prior art methods and which completely eliminate the use of sand-blasting.

A further object is the provision of a method of preparing metal surfaces for the application of ceramic coatings, which uniformly prepares the surface to be coated regardless of the complexity of the article or surface and without distortion, thinning, or in any way materially changing the dimension of the article.

Another object of the invention is to provide methods of surface treatment of metals for promoting superior adherence of ceramic coating thereto even after said surfaces have been subjected to sand-blasting.

Still another important object is the provision of methods for developing superior adherence between basis metals and ceramic coatings at firing temperatures substantially lower than those previously necessary.

Yet another object is the provision of methods for surface treating metals prior to coating with ceramic which requires none of the bulky and cumbersome equipment associated with prior art methods.

A further object of the invention is to provide a method of treating metals containing at least 5% chromium so as to substantially completely convert the chromium content in the exposed surfaces of said metal to a microscopically thin layer of chromic oxide (Cr_2O_3).

These and subordinate objects, the manner in which they are fulfilled and additional advantages of the invention will be readily apparent to those familiar with the art from the following description and subjoined claims.

In its broader aspects, the process contemplated by this invention involves the creation of a carefully controlled oxide film on the surfaces of the metal to which a ceramic coating may be applied. This is accomplished by causing the surface of the basis metal to combine with free atomic (nascent) oxygen, 0°, and thus convert the surface of the metal to a microscopically thin, slightly porous oxide film. Inasmuch as the type of metals to be treated according to the invention, namely chromium steels, stainless steels, the super alloys, and like metals having a chromium content of at least 5%, vary in composition, the precise chemical composition of the oxide film depends on the particular metal treated. However, inasmuch as these metals usually contain substantial quantities of iron, chromium and nickel this film generally consists essentially of chromium oxide, with some iron oxide and nickel oxide spinels.

It is an important and unique characteristic of this film that the chromium oxide therein is almost exclusively Cr_2O_3 as opposed to chromic anhydride (CrO_3). Inasmuch as this film is formed from the basis metal, it is greatly superior to any type of externally applied surface film. The characteristics of this film, particularly its slight porosity, are such that a ceramic coating subsequently applied thereto forms a bond far superior to that

which may be obtained by prior art methods of surface treatment.

It has been found that in order to achieve an optimum oxide of the type contemplated by the invention, it is necessary to supply nascent oxygen to the metal surface. While oxide films have been obtained by firing the metal in a furnace supplied with molecular oxygen, either wet or dry, this process is not consistent nor is the oxide uniform over the surface. The novel process contemplated by the present invention can best be described as a chemical treatment which creates the oxide film on the metal by controlled oxidation. As will hereinafter be seen, all chemicals used in the process are generally classified as oxidizers and, furthermore, as agents which liberate oxygen during decomposition by heat. The following equation will generally represent the decomposition reaction:

$$MO_x \xrightarrow{\text{HEAT}} MO_{x-1} + 0^\circ$$

In the above generalized equation MO_x may represent either an ion or a compound. It has been discovered, however, that only a few of the materials falling in the general class of oxidizers are useful for this purpose. For example, ammonium molybdate produces a uniform oxide, but the oxide film is only partially satisfactory in developing great adherence with the subsequent ceramic coat. Sodium nitrate, sodium chromate, sodium dichromate and ammonium nitrate produce a highly unsatisfactory, loose, black scale which does not adhere tightly to the base metal.

It has been discovered, however, that chromic acid when applied according to one embodiment of the invention as will hereinafter be described and chromic anhydride (anhydrous chromic acid) according to another embodiment of the invention give highly satisfactory results. These processes will now be described.

Chromic acid process

In this form of the invention, a chromic acid solution of from 5 to 20% by weight is provided and used at a temperature of 160 to 200° F. If it is desired to utilize the solution at room temperature, a concentration of 10 to 20% by weight is required. The part to be treated is degreased thoroughly by any standard method such, for example, as scaling for from 1 to 3 minutes at 1700° F. followed by a white pickle and water rinse.

The part is then dipped in the chromic acid solution (either hot or cold as explained above) just long enough to assure complete wetting. The wetted part then is fired at from 1500° F. to 1800° F. for from 30 seconds to 20 minutes, or in any event long enough to bring the part to heat and hold it for 30 seconds. Experience in treating a number of parts of various size and thickness has shown that an average time of from 3 to 5 minutes is usually most satisfactory.

If the concentration of the acid solution is too low, the fired part will have a bluish tinge, while too high a concentration will produce a film displaying thickened greenish beads or waves, which may be removed by brushing. The optimum color of the fired part is a light straw.

Following the dip, the part should be fired within an hour because the chromic acid will deteriorate if allowed to stand over a longer period.

The part after firing is ready for the ceramic coating cycle, which can follow any standard specification such, for example, as spraying, slushing, or dipping the part in the desired ceramic coating slip followed by drying and firing at an appropriate temperature as required by the particular ceramic coating being applied.

It should be understood that, should the first acid dip and firing fail to obtain the desired oxide and develop a uniform coating over all surfaces, the part may be redipped and refired until the desired oxide is developed before proceeding with the ceramic coating step. The temperature limits, namely 1500 to 1800° F., for firing the part after the acid dip, are essential to obtain the desired decomposition of the chromic acid and consequently the creation of the desired oxide film as hereinafter explained. At lower than critical temperatures insufficient nascent oxygen is released to form an oxide of the basis metal and a coating which is predominantly chromic anhydride (CrO_3) is merely deposited on the basis metal. Such a coating does not form a satisfactory surface for the application of ceramic coatings.

Chromic anhydride process

In this embodiment of the invention, the part to be treated is thoroughly degreased as in the chromic acid treatment discussed above and is then placed, along with a small amount of loose chromic anhydride powder, in the furnace or oven. The part is then heated to the same temperatures and for the same periods as in the chromic acid process, namely 1500 to 1800° F. for from 30 seconds to 20 minutes. At temperatures of aproximately 1500° F. and above the vapors of the chromic anhydride react with the basis metal producing the stable chromic oxide as described in the chromic acid process.

This embodiment of the invention, in general, will not prove as satisfactory as the dip method when treating complex parts inasmuch as the vapors will not seek out hidden areas. In dealing with simple parts, however, the anhydride method has the distinct advantages of eliminating dip tanks and the necessity of preparing the chromic acid solution.

In either method the chemical reaction by which the oxide layer is formed is essentially the same, that is, the chromic anhydride (CrO_3) decomposes at the temperatures involved as indicated in the following equation:

$$2CrO_3 \xrightarrow{\text{heat}} Cr_2O_3 + 3O^0 \text{ (3 atoms of nascent oxygen)}$$

The atoms of nascent oxygen released by this decomposition react with the chromium atoms at the surface of the basis metal to form Cr_2O_3, with the ferrous content of the metal to form iron oxide and with the nickel content (if any) to form nickel oxide spinels. From a consideration of the foregoing description of the action of the chromic acid and chromic anhydride, it will be appreciated that firing temperatures within the limits stated are essential to the production of the desired oxide layer. At lower temperatures the chromic anhydride is not or is only partially decomposed with the result that a coating consisting of a combination of chromic oxide and chromium anhydride is merely deposited on the surface of the base metal. According to the novel process described herein, carried on at the proper temperatures, the oxide film is not merely a layer added to the base metal but rather is, in fact, formed from the base metal.

This microscopically thin, slightly porous surface is an ideal base for the subsequent application of ceramic coatings which, upon firing, interdiffuse with the oxide film and are thus strongly bonded to the base metal.

It has been found that by the use of the novel process disclosed herein, it becomes possible to develop a far superior bond between the basis metal and a ceramic coating at substantially reduced firing temperatures. For example, one coating tested normally requires a firing temperature of 1750° F. when applied to stainless steel prepared by prior art method. However, when applied to stainless steel which has been treated according to the present invention, this same coating develops a much superior bond when fired at only 1650° F. It is believed that this reduced firing temperature is made possible because of the porosity of the surface oxide film developed on the basis metal. This porous film is an ideal surface over and into which the ceramic flows during firing and to which it strongly adheres while still far more viscous than possible when a surface roughened, as by sandblasting or other prior art means, is provided.

It is well known in the art that a slight oxidizing of the basis metal during firing thereon of a ceramic coating

is desirable in that it permits better adherence. However, many alloys, such for example as Inconel, do not readily oxidize at the firing temperatures normally required for ceramic coatings. Consequently it has been deemed necessary and has been common practice in the past to substantially increase these temperatures, far beyond those necessary for proper firing of the coating merely to assure such oxidation and subsequent satisfactory bonding. Accordingly it will be appreciated, that by using the methods herein disclosed, superior bonding of ceramic coatings at lower temperatures is obtained not only because the previously provided oxide film is particularly adapted by reason of its porosity to permit adherence, but also because the need for a temperature induced oxidation of the basis metal during firing of the ceramic coating is eliminated.

The invention may be embodied in other specific forms without departing from the spirit of essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by the United States Letters Patent is:

1. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium comprising the step of bringing into contact with said surfaces a chromium-oxygen compound selected from the group consisting of chromic acid and chromium anhydride at a minimum temperature of approximately 1500° F., whereby said compound decomposes to release nascent oxygen for oxidizing said surfaces and converting the chromium content thereof to chromic oxide.

2. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium comprising applying chromic acid solution to said surfaces and heating said surfaces to a temperature of at least 1500° F.

3. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium comprising wetting said surfaces with a 5 to 20% aqueous solution of chromic acid, heating said metal to a surface temperature of between 1500 and 1800° F.

and maintaining said temperature for at least 30 seconds.

4. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium, comprising immersing said alloys in a solution of 5 to 20% by weight of chromic acid at a temperature of between 160 to 200° F. and then heating said alloys to a surface temperature of from 1500 to 1800° F.

5. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium comprising heating said alloys in an enclosure to a minimum surface temperature of approximately 1500° F. in the presence of chromic anhydride.

6. A method for converting to an oxide film the exposed surfaces of metal alloys containing at least 5% chromium comprising heating said alloys in an enclosure to a surface temperature of from 1500 to 1800° F. in the presence of chromic anhydride and maintaining said temperature for at least 30 seconds.

7. A method for applying ceramic coatings to basis metals containing at least 5% chromium comprising, the steps of bringing said surfaces into contact with a chromium-oxygen compound selected from the group consisting of chromic acid and chromic anhydride, at a temperature of from 1500 to 1800° F.; maintaining said temperature for at least 30 seconds; and subsequently applying and firing the ceramic coating.

8. A method of coating with a ceramic a metallic part containing at least 5% chromium comprising the steps of forming from said basis metal, a thin porous film of Cr_2O_3 on the surface thereof; subsequently applying said ceramic to the surface of said part and thereafter firing said part.

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