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METHOD OF BRIGHT HEAT-TREATING METALS

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The invention relates to a novel method of bright heat-treating metals.

In the art of heat treating metals, such as stainless steels containing up to 12% chromium and age hardening ferrous alloys containing chromium, and other types of alloys, it is necessary to operate at temperatures above 1700° F. in order that the chromium alloy member being treated will emerge bright. Discoloration that occurs at lower temperatures is due to oxidation of the surfaces of the member being treated. It is generally believed that the temperature below which bright work cannot be obtained in conventional heat-treating furnaces is dependent upon the purity, particularly H_2O content, of the protective atmosphere it is the practice to use in the furnace. This phenomenon of bright work at high temperatures and discoloration or oxidation at lower temperatures is attributed to the change with temperature of the equilibrium of the reaction:

$$\text{chromium} + \text{water} \rightleftharpoons \text{chromium oxide} + \text{hydrogen}$$

A high temperature supposedly shifts this equilibrium to the left. To reduce the water content of a protective atmosphere to a value which would produce bright chromium steels in a temperature range below 1,700° F. would be commercially impractical.

It is often desirable to stress-relief anneal stainless steel members containing up to 12% chromium at temperatures ranging from 1000° F. to 1200° F. and at the same time to produce a bright surface thereon. It is our belief that the oxidation that occurs at temperatures ranging from 1000° F. to 1200° F. is caused by an adsorbed film of air carried on the surface of the work into the hot zone of the treating furnace.

An object of this invention is to provide a method for heat treating metals wherein the metal is coated with a liquid organosiloxane before heating in order to prevent the metal from carrying an adsorbed film of air in the heating zone and thereby become discolored by oxidation.

A further object of this invention is to provide a method for heat treating metals wherein the metal is coated with a liquid organosiloxane before heating to prevent surface discoloration of the metal caused by oxidation during heat treatment.

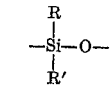
Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

We have discovered that bright work can be produced in heat treating chromium containing ferrous metallic members at temperatures below 1700° F., by coating the metals with a liquid organosiloxane or silicone polymer before their entry into the hot zone of a furnace. The coating of a liquid silicone polymer prevents the members from carrying an adsorbed film of air into the hot zone of the furnace.

The chromium alloy members are coated with the liquid silicone polymer by any suitable means such as dipping, spraying, flowing, brushing, etc., and are then introduced while still wet into a heated purging chamber

having a protective atmosphere flowing therethrough. The flow of the protective atmosphere is countercurrent to the path of travel of the chromium alloy members from the purging chamber into the annealing zone proper of the furnace, and thus the liquid silicone polymer is removed from the members before it reaches the annealing zone. In this manner, the liquid silicone polymer does not contaminate the atmosphere in the hot zone of the furnace.

The term "liquid silicone polymer" is given to polymeric compounds having a characteristic straight chain-forming unit



where R and R′ are the same or different organic radicals joined directly to the silicon atom through carbon and the term "silicone polymer" has this meaning where employed in this specification and in the claims. These liquid silicone polymers contain from 1.8 to 3.0 organic groups per silicon atom. These organosiloxane polymers are usually formed through the molecular condensation to siloxanes of organosilanols of the type formula: $R_nSi(OH)_{4-n}$ wherein R comprises substituted or unsubstituted mono-, di- or tri-alkyl, aryl, aralkyl, alkaryl substituents or mixtures thereof, such as methyl, ethyl, propyl, butyl, phenyl, benzyl, tolyl, naphthyl, etc. and n is an integer from about 2 to 3. These silanols can be obtained for instance by the hydrolysis of the corresponding halogenosilanes or alkoxysilanes. Specific types of silanols include trimethylsilanol, triethylsilanol, diethylsilanediol, diphenylsilanediol, etc.

While intermolecular condensation comprises one method of forming the linear and cyclic organosiloxanes or silicone polymers useful in this invention, they can also be obtained by other methods.

Such liquid silicone polymers exist in widely varied physical form, some being thin liquids, others having the form of thicker oils, depending on the proportion and character of the organic radicals present and on the conditions to which the polymer was subjected during its formation.

While certain of these polymers are somewhat more effective in the practice of this invention than are others, all of the liquids in the class will produce the desired result so long as the members can be coated therewith. The majority of liquid silicone polymers commercially produced contain at least one of methyl, ethyl or phenyl groups as the organic radicals.

Any of the conventional protective atmospheres may be used in practicing this invention. Those commonly used in the art are (1) chemically pure hydrogen and (2) chemically pure nitrogen, which is totally inert, or (3) mixtures of H_2 and N_2. A protective atmosphere finding extensive use is produced by dissociating commercial ammonia which yields, when properly processed, an extremely pure gas which is very low in water content. It contains one part by volume nitrogen and three parts of hydrogen. Dissociated ammonia must be very dry for successful use as a protective atmosphere. A moisture content of not more than 0.03 precent by volume (dew point of —35° C.) is required, and the drier the gas the better.

If necessary to thin the liquid silicone polymer in order to coat the meter members more easily, any number of suitable well known solvents may be used such as carbon-tetrachloride, benzene, xylene, N-amyl alcohol, ethyl acetate and others. In practicing this invention, the liquid silicone polymer solutions should contain at least 50% by weight liquid silicone polymer. It has been found that with the use of solutions containing less than

50% by weight silicone polymer that an occasional sample would show slight discoloration at sharp corners or projections. In most of our work, both the liquid silicone polymers and their solutions had a viscosity of about 200 centistokes at 25° C., but the viscosity may be varied within practical limits as desired.

Example

The following example is illustrative of the practice of this invention. A turbine compressor blade of stainless steel containing about 12% chromium was dipped in a solution comprising dimethyl silicone and benzene. The solution contained 60% by weight of silicone polymer and had a viscosity of 200 centistokes at 25° C. The silicone polymer incorporated in the solution was obtained from the Dow-Corning Corporation under the trade name "Dow-Corning Fluid 200." The coated compressor blade was placed while wet in a purging zone having a protecting atmosphere of dissociated ammonia flowing therethrough. The dissociated ammonia had a dew point of —45° C. The compressor blade was passed from the purging zone into the annealing zone of a furnace which was maintained at a temperature of from 1000° F. to 1200° F. The liquid silicone solution was completely removed from the compressor blade by the time it reached the annealing zone of the furnace. After the compressor blade was annealed, it was removed from the furnace by way of a cooling zone. The annealed blade had a bright surface with no discoloration present.

While this invention is disclosed herein as applying specifically to chromium containing ferrous alloys, it is to be understood that it is applicable in the heat treatment of any readily oxidizable metal such for example as those disclosed in the patent to Scott et al., Serial No. 2,519,406, issued August 22, 1950.

Since certain changes may be made in the above description and different modes of applying the principles of the invention may be made without departing from the spirit and scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. In the method of heat-treating oxidizable metals, the steps comprising coating the metal with a liquid silicone polymer having a ratio of from 1.8 to 3.0 organic groups per silicon atom, the organic groups being attached to the silicon atoms by carbon silicon linkages, and being selected from at least one of the group consisting of methyl, ethyl, and phenyl radicals, introducing the coated metal into a hot purging chamber having a non-oxidizing atmosphere flowing therethrough in such manner as to remove the silicone coating from the metal, and thereafter moving the metal into the heat-treating zone of a furnace.

2. In the method of heat-treating oxidizable metals, the steps comprising coating the metal with a liquid silicone polymer having a ratio of from 1.8 to 3.0 organic groups per silicon atom, the organic groups being attached to the silicon atoms by carbon silicon linkages, introducing the coated metal into a hot purging chamber having a non-oxidizing atmosphere flowing countercurrently therethrough to remove the silicone coating from the metal, and thereafter moving the metal into the heat-treating zone of a furnace.

3. The method of claim 1 in which the liquid silicone polymer is a dimethyl silicone.

4. The method of claim 1 wherein the liquid silicone polymer is dissolved in a volatile organic solvent to provide a solution of a viscosity of about 200 centistokes at 25° C.

5. The method of claim 1 in which the non-oxidizing atmosphere has a dew point no higher than minus 35° C.

6. The method of claim 1 in which the metal is an alloy comprising iron and chromium and the hot zone of the furnace is maintained at a temperature of from 1000° F. to 1200° F.

7. The method of claim 1 in which the liquid silicone polymer is present in a solution in a volatile organic solvent in an amount of at least 50% by weight silicone polymer.

8. In the method of bright heat treating ferrous members containing chromium, the steps comprising coating the member with a liquid silicone polymer having a ratio of from 1.8 to 3.0 organic groups per silicon atom, the organic groups being attached to the silicon atoms by carbon silicon linkages and being selected from at least one of the group consisting of methyl, ethyl, and phenyl radicals, the liquid silicone polymer having a viscosity of substantially 200 centistokes, introducing the coated member into a hot purging chamber having a protective atmosphere flowing therethrough countercurrently to the path of travel of said member whereby the liquid silicone polymer is removed from the member, the protective atmosphere having a dew point of substantially minus 45° C., and thereafter moving the member into the heat-treating zone of a furnace maintained at a temperature of from 1000° F. to 1200° F.

9. The method of claim 8 in which the liquid silicone polymer is a dimethyl silicone.

10. The method of claim 8 in which the liquid silicone polymer is present in a solution in an amount of at least 50% by weight silicone polymer.

11. In the process of bright heat-treating oxidizable metallic members in a heating zone maintained at temperatures between 1000° F. to 1200° F., the improvement which comprises applying a coating of a liquid silicone polymer to the members to prevent the same from carrying a film of air into the heating zone, passing the coated members into a purging zone having a protective atmosphere flowing therethrough at a rate sufficient to remove the silicone coating from the members, thereafter annealing the members in the heating zone at temperatures between 1000° F. to 1200° F., and removing the annealed members from the heating zone.

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