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METAL TREATMENT

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ABSTRACT OF THE DISCLOSURE

A method of heat treating metal workpieces in a molten bath of borate glass consisting on a 100 parts weight basis of from 71.8 to 85.5 parts by weight of boric oxide, from 5.5 to 10.7 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium and lithium, and from 9.0 to 17.5 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium and zirconium.

This invention relates generally to the treatment of metals to develop improved properties therein, and specifically concerns a method of heat-treating metals and also compositions for use in connection with such heat-treating.

Basically, the method of this invention employs the steps of immersing the to-be-treated metal in a bath of molten borate glass having a preferred composition, maintaining the metal in such bath a sufficient time to develop the desired elevated temperature in the metal, and afterwards cooling the heated metal to ambient temperature following removal from the bath to thereby obtain the improved physical properties. No step of coating the metal prior to heating is required. A film of molten glass adheres to the metal on removal from the bath and forms a protective coating that prevents oxidation during transfer and cooling in air. In those instances where the metal is to be cooled at rapid rates, as by air or liquid quenching, the retained film provides less resistance to heat transfer than other known glass heat-treating compositions. The nature of the preferred composition used is such that it may be completely removed from the heat-treated metal subsequent to cooling by water-washing; also should residual portions remain, the metal surface will not be subjected to intergranular corrosion as in the case of residual neutral salt materials. Since the preferred material is water-soluble, the protective coating may be completely removed as part of the cooling step if water-quenching is involved. Metals processed in accordance with this invention, particularly titanium and its alloys in oxygen-sensitive metals, obtain improved properties in comparison with the properties developed through the practice of other bath heat-treating methods. Also, many processing advantages may be realized from use of the preferred borate glass compositions in heat-treating in comparison to the use of neutral salts, silicate-containing glasses, and other known heat-treating media.

A primary object of this invention is to provide a heat-treating method that may be used throughout a comparatively wide range of elevated heat-treating temperatures to produce heat-treated metals that are not subjected to decarburization, oxidation, chemical attack, and like surface phenomena during processing.

Another object of this invention is to provide a heat-treating method that develops a retained protective coating on heat-treated metals on removal from the heat-treating medium at elevated temperatures, such protective coating having the further performance characteristic of not significantly impeding cooling rates when the metals are quenched to ambient temperatures particularly by immersion in liquid cooling media.

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A still further object of this invention is to provide a heat-treating method utilizing a composition that may be used throughout a comparatively wide range of elevated heat-treating temperatures, such method further involving the use of a water-soluble heat-treating composition.

Another object of this invention is to provide a heat-treating method that may be followed by water-washing to remove residual heat-treating medium from the metal, such heat-treating medium in the absence of complete removal also being incapable of causing intergranular corrosion in the treated metal.

Another object of the invention is to provide a heat-treating composition that is chemically and physically stable throughout a comparatively wide range of heat-treating temperatures, such range extending from 1450° F. to 2350° F. approximately, and that does not introduce decarburization, oxidation, chemical attack, or like surface phenomena into metals heat-treated therein.

Another object of this invention is to provide a heat-treating composition that is chemically and physically stable over prolonged periods of time when maintained in a molten state at temperatures in the range of 1450° F. to 2350° F. approximately.

Another object of the invention is to provide a heat-treating composition that may be used without modification in the heat-treating at elevated temperatures of both ferrous and non-ferrous metals.

Another object of the invention is to provide a heat-treating composition that may be used throughout a heat-treating temperature range of from 1450° F. to 2350° F. approximately, and that is water-soluble at ambient temperatures.

A still further object of this invention is to provide a heat-treating composition that by reason of viscosity, surface tension, and thermal conductance properties at elevated temperatures functions to develop a retained protective film on metals removed therefrom at temperatures in the range of 1450° F. to 2350° F. approximately, such retained film being characterized by the fact that it does not have a significant insulating or heat transfer impeding effect during rapid cooling to ambient temperatures.

Another object of the invention is to provide a heat-treating composition that can be manufactured using known techniques and that is comparatively inexpensive to produce and use.

Other objects of the invention will become apparent from consideration of the specification as a whole.

COMPOSITION

The heat-treating composition that is utilized in the practice of this invention is essentially a water-soluble borate glass. Specific compositions which have been developed are given in the following Examples I through III. In each instance the composition calculated oxide content is given on a parts by weight basis; the molecular ratios involved are given parenthetically.

Example 1

Constituent	Parts by Weight	Molar Ratio
Boric Oxide (B ₂ O ₃)	82.8	3.4
Alkali Metal Oxide (Na ₂ O)	6.5	0.3
Viscosity Control Oxide (Al ₂ O ₃)	10.7	0.3
	100.0	

Example II

Constituent	Parts by Weight	Molar Ratio
Boric Oxide (B ₂ O ₃)	71.8	3.0
Alkali Metal Oxide (Na ₂ O)	10.7	0.5
Viscosity Control Oxide (Al ₂ O ₃)	17.5	0.5
	100.0	

Example III

Constituent	Parts by Weight	Molar Ratio
Boric Oxide (B_2O_3)	85.5	3.5
Alkali Metal Oxide (Na_2O)	5.5	0.25
Viscosity Control Oxide (Al_2O_3)	9.0	0.25
	100.0	

The above compositions may be compounded by properly smelting, firing, and quenching different combinations of batching ingredients using conventional materials and process methods. The following Table I indicates several specific batch formulations that may be utilized to produce the glass of Example I.

TABLE I

Ingredient	Formulation No.				
	1	2	3	4	5
Boric Acid			68.3		83.8
Boric Oxide	82.8	68.1		75.0	
Anhydrous Borax		21.2			
Hydrous Borax			22.5		
Aluminum Oxide		10.7			6.1
Hydrated Alumina			9.2	14.9	
Sodium Aluminate	17.2				
Sodium Carbonate				10.1	
Sodium Nitrate					10.1
	100.0	100.0	100.0	100.0	100.0

All ingredients are stated on a parts by weight basis. The materials are preferably of a quality corresponding to the commercial grades used in making glass and porcelain frits. Normally, smelting is accomplished at 2000° F., firing at 1850° F., and quenching with chilled rollers. Care must be taken to avoid water-quenching as the preferred compositions are clearly water-soluble. Continuous as well as batch processing may be used.

In making the preferred heat-treating compositions, certain trace elements (copper, silver, gold, zinc, cadmium, lead, manganese, cobalt, and nickel) are not generally permitted in amounts exceeding 0.005% each. Other frequent glass-making contaminants such as lithium, magnesium, calcium, potassium, strontium, titanium, zirconium, and iron, in other than oxide form, may be permitted in amounts up to 0.05% each.

For most heat-treating purposes, the example compositions are satisfactory if furnished in solid flake or fritted form. Also, the glasses are preferably non-tinted.

Care is taken to control the formulation of the compositions of this invention in several respects. First, composition is controlled as to acidity-alkalinity. With respect to a solution containing 10 grams of the prescribed borate glass dissolved in 200 cubic centimeters of distilled water, the obtained hydrogen ion concentration should preferably range in pH value from approximately 5.9 to 7.1. The material of Example I has a pH rating of 6.0 to 6.25 and is essentially neutral. The Examples II and III materials are characterized as producing pH ranges of 7.0 to 7.1 and 5.9 to 5.95, respectively; such values essentially represent the limits of alkalinity and acidity that have been established on the basis of experimentation to date. In accomplishing such control it is preferred that an alkali metal oxide such as the sodium oxide constituent be utilized. However, other constituents such as potassium oxide or lithium oxide may be used as a substitute for sodium oxide and equivalent metallurgical results will be obtained.

Second, the composition is controlled as to viscosity and surface tension properties at temperatures. Generally, the compositions detailed above may be used in molten form for heat-treating operations involving elevated temperatures in the range of 1450° F. to 2300° F. If a substitute material is desired for the aluminum oxide, zirconia (ZrO_2) and titania (TiO_2) are generally suitable. Possibly other intermediate metal oxides may be used. Also, basic modifier oxides such as magnesia (MgO) may be included in the composition in lieu of alumina to

assist in obtaining the desired viscosity control and surface tension regulation. The purpose of viscosity control and surface tension regulation is to cause a retained film of composition to adhere to immersed heat-treated metals on removal, such film protecting surface metal from oxidation or other forms of deterioration during transfer and subsequent cooling particularly in air environments. Also, the retained film should be sufficiently thin so as to not impede required heat transfer rates in subsequent cooling operations, especially if rapid cooling as by quenching in air or liquid will be involved. With reference to the Example II and III compositions, the amount of included alumina is established for heat-treating at heat-treating temperatures in the upper and lower portions, respectively, of the previously-identified 1450° F. to 2300° F. overall range. As a general rule, the amount of viscosity control oxide (alumina) included in the composition should not exceed approximately 11% on a parts by weight basis. Amounts above this limit generally adversely affect the water solubility of the neutralized borate glass.

Also, quantitative standards have been established for verifying obtained viscosity and surface tension property control. Such is accomplished by use of fusion flow measurements. In the form used in support of this invention, fusion flow is determined using a 5 gram sample of the heat-treating composition in a -20 to +40 mesh fritted form, moistened with 4 drops of distilled water, and compressed into a 1" diameter button using 2,000 pounds per square inch pressure for 5 seconds. The button, after drying at 250° F. to remove moisture, is placed on an essentially horizontally positioned flat panel of Type 302 stainless steel and fired at 1625° F. for 3 minutes. After cooling, the degree of flow experienced by the composition sample is determined on the basis of the increase of the average diameter of the flowed material over the original button diameter. Thus, a 1" diameter button having a 1½" diameter in the fired and solidified condition has a diameter ratio of 1.5 (150%) and a fusion flow value of 50%. The flowed dimension is established as the average of two specific dimensions taken at right angles to each other. In terms of the compositions specified by the examples, fusion flow values in the range of approximately 90% to 150% are experienced. Example I materials have a fusion flow value in the range of 110% to 130%; Example II and III compositions have higher and lower viscosities at temperature. Thus, fusion flow values of 90% and 110% are normally experienced with the Example II composition and values of 120% to 150% with the Example III material.

PROCESS STEPS

From a processing standpoint, this invention generally involves the sequential steps of:

(1) Immersing the metal that is to be heat-treated in a bath of molten borate glass having the composition described herein preferably while the metal is essentially at ambient room temperature and with the bath temperature equal to or above the elevated temperature to be attained in the metal,

(2) Maintaining the metal in the molten bath a sufficient time to attain in the metal the desired elevated temperature necessary for accomplishing the heat-treating objective,

(3) Withdrawing the metal after it has reached the desired elevated temperature from the molten bath with a retained film of composition that serves as a protective coating during subsequent transfer or cooling of the metal in an air environment,

(4) Cooling the heated metal to ambient temperature at the desired cooling rate, often using an air-quenching or liquid-quenching technique, and

(5) Removing the retained film preferably by immersing or washing the heat-treated metal in water.

Specific examples of the use of the heat-treating invention are given by means of the following Examples IV

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through XI. As will be noted, the invention has application to different metals, including ferrous and non-ferrous alloys, to different heat-treating objectives, including austenitizing, stress relieving, solution annealing, and the like, and to different time and temperature parameters. In each instance, however, the process utilizes the previously described heat-treating composition.

Example IV

A specimen of 4Al-3-Mo-1V titanium alloy in 0.063" thick sheet form was heated to a temperature of 1625° F. by immersion for 10 minutes in a molten bath of Example I borate glass heat-treating composition, subsequently removed with a retained protective coating, and afterwards water-quenched by immersion within 10 seconds in room temperature water.

The specimen obtained a hardness of Rc 30-31. The specimen was thereby solution heat-treated and put in a condition suitable for subsequent age-hardening to develop maximum obtainable properties. No corrosion of the alloy similar to that experienced by heat-treatment in neutral salts existed. Further, the grain structure that was obtained was superior to grain structures associated with heat-treatment in silicate glass followed by water-quenching. The retained protective coating was removed by immersing the metal in hot water (140° F.) for approximately 10 minutes immediately after quenching had been accomplished.

Example V

The specimen and process steps of this example corresponded to the specimen and process steps of Example IV except that the heat-treating composition employed was the water-soluble borate glass of Example II. The results which were obtained correspond to those obtained in connection with the Example IV method except that the metal hardness was determined to be Rc 32-33.

Example VI

The specimen and process steps utilized in connection with this example corresponded to the specimen and process steps detailed in connection with Examples IV and V except that the heat-treating composition utilized was the Example III borate glass. The metallurgical results which were obtained in connection with this example corresponded to the metallurgical results of Examples IV and V except that the metal hardness was Rc 31-32.

Example VII

A specimen of H-11 ultra-high-strength alloy steel in 0.063" thick sheet form was heat-treated by immersion in a bath of molten Example I material at a temperature of 1850° F. for 20 minutes for austenitizing purposes. The specimen was afterwards withdrawn from the molten bath with a retained protective coating and then air-cooled to ambient room temperatures. The specimen was also subsequently processed in hot water for approximately 10 minutes to remove the previously-retained protective film. A careful metallurgical examination established that the metal was properly heat-treated to develop maximum tensile strength and was completely free of decarburized metal at exterior surfaces.

Example VIII

Specimen forgings of Types 4130 and 4140 low-alloy structural steels were heat-treated in accordance with this invention for the purpose of restoring decarburized surface metal to a preferred non-decarburized condition and also for the purpose of austenitizing. Each specimen forging had typical thickness in the range of ½" to 1". The forgings were immersed in a bath of molten borate glass having a composition corresponding to that of Example I at a temperature of 1600° F. for 2 hours. The parts were withdrawn with a thin retained film of composition and afterwards immediately cooled by quenching in oil in a conventional manner. Subsequently, the re-

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tained protective film was removed by processing in hot water (140° F.) for 10 to 15 minutes to obtain complete film removal. The decarburized surface metal in the specimen forgings had been restored to a proper metallurgical condition which exists interiorly of the decarburized surface region.

Example IX

A specimen of TZM molybdenum alloy was processed in accordance with this invention for stress relieving purposes. The specimen, in 0.080" thick sheet form, was immersed in a bath of molten Example I composition for a period of one hour and obtained an 1800° F. temperature. The specimen, with a retained protective coating, was afterwards cooled by air-quenching to ambient temperature and then metallurgically examined. The desired grain structure existed within the heat-treated material, and further no corrosion of the type associated with heat-treating in air or neutral salt media existed.

Example X

A specimen of Type 410 low-alloy stainless steel was immersed in 0.080" thick sheet form, in a bath of molten Example I composition at a temperature of 1825° F. for 15 minutes for austenitizing purposes. The specimen was afterwards removed from the molten borate glass bath with a retained film and then immediately cooled by an oil-quenching step. Again, the specimen possessed the desired metallurgical structure without any evidence of decarburization.

Example XI

A specimen of René 41 alloy, in 0.050" thick sheet form, was heat-treated in a bath of molten Example I material at a temperature of 1950° F. for 10 minutes for solution heat-treating purposes. The material was afterwards removed with a retained film of composition and cooled by water-quenching to ambient temperature. Cooling was continued a sufficient time to also accomplish film removal as part of the cooling operation. The part was afterwards examined and it was determined that no metallurgical deficiencies existed. Proper hardness and tensile qualities were fully developed without adverse effects being caused by the heat-treatment procedure.

Use of the instant invention in connection with alloy materials that have been worked so as to cause a loss of ductility and with respect to alloy materials that require heat-treatment from an essentially annealed condition is advantageous.

I claim:

1. In a method of heat-treating a metal to develop a temperature therein in the temperature range of approximately 1450° F. to 2350° F. by heat transfer in a liquid medium prior to withdrawal and subsequent cooling, the sequential steps of:

- (a) Immersing said metal in a bath of molten water-soluble borate glass,
- (b) Retaining said metal in said bath a sufficient time to raise the temperature of said metal to a temperature in the temperature range of approximately 1450° F. to 2350° F.,
- (c) Removing said metal from said bath with a thin film of said molten borate glass retained thereon, and
- (d) Afterwards cooling said metal,

said borate glass consisting on a 100 parts weight basis of from 71.8 to 85.5 parts by weight of boric oxide, from 5.5 to 10.7 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium, and from 9.0 to 17.5 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium, and zirconium.

2. The method defined by claim 1, wherein said borate glass consists of 82.8 parts by weight of boric oxide, 6.5 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium,

and 10.7 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium, and zirconium.

3. The method defined by claim 1, wherein said borate glass consists of 82.8 parts by weight of boric oxide, 6.5 parts by weight of sodium oxide, and 10.7 parts by weight of aluminum oxide.

4. In a method of heat-treating a metal to develop a temperature therein in the temperature range of approximately 1450° F. to 2350° F. by heat transfer in a liquid medium prior to withdrawal and subsequent cooling, the sequential steps of:

(a) Immersing said metal in a bath of molten water-soluble borate glass,

(b) Retaining said metal in said bath a sufficient time to raise the temperature of said metal to a temperature in the temperature range of approximately 1450° F. to 2350° F.,

(c) Removing said metal from said bath with a thin film of said molten borate glass retained thereon,

(d) Cooling said metal, and

(e) Removing said thin film of retained borate glass by immersing said metal in water,

said borate glass consisting on a 100 parts weight basis of from 71.8 to 85.5 parts by weight of boric oxide, from 5.5 to 10.7 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium, and from 9.0 to 17.5 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium, and zirconium.

5. The method defined by claim 4, wherein said borate glass consists of 82.8 parts by weight of boric oxide, 6.5 parts by weight of sodium oxide, and 10.7 parts by weight of aluminum oxide.

6. In a method of heat-treating a metal to develop a temperature therein in the temperature range of approximately 1450° F. 2350° F. by heat transfer in a liquid medium prior to withdrawal and subsequent cooling, the steps of:

(a) Immersing said metal in a bath of molten water-soluble borate glass,

(b) Retaining said metal in said bath a sufficient time to raise the temperature of said metal to a temperature in the temperature range of approximately 1450° F. to 2350° F.,

(c) Removing said metal from said bath with a thin film of said molten borate glass retained thereon, and

(d) Simultaneously cooling said metal and removing said film of retained borate glass by immersing said metal in water,

said borate glass consisting on a 100 parts weight basis of from 71.8 to 85.5 parts by weight of boric oxide, from 5.5 to 10.7 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium, and from 9.0 to 17.5 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium, and zirconium.

7. The method defined by claim 6, wherein said borate glass consists of 82.8 parts by weight of boric oxide, 6.5 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium, and 10.7 parts by weight of viscosity and surface tension control oxide from the group consisting of the oxides of aluminum, titanium, and zirconium.

8. In a method of heat-treating a metal to develop desired physical and metallurgical properties and involving the steps of heating the metal to a temperature in the temperature range of approximately 1450° F. to 2350° F. and in a liquid medium prior to withdrawal and subsequent cooling, the step of heating said metal in molten water-soluble borate glass consisting on a 100 parts weight basis of from 71.8 to 85.5 parts by weight of boric oxide, from 5.5 to 10.7 parts by weight of alkali metal oxide from the group consisting of the oxides of sodium, potassium, and lithium, and from 9.0 to 17.5 parts by weight of viscosity and surface tension control oxide selected from the group consisting of the oxides of aluminum, titanium, and zirconium.

References Cited

UNITED STATES PATENTS

2,238,777	4/1941	Lemmers et al.	106—47 X
2,321,917	6/1943	Jenkins et al.	148—14
2,959,503	11/1960	Lindson	148—20
3,061,752	10/1962	Banks	106—47 X
3,150,281	9/1964	Bishay	106—47 X
3,158,515	11/1964	Michael	148—28 X

FOREIGN PATENTS

698,425	10/1953	Great Britain.
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