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COATED ALLOYS

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This invention deals with the coating of metals of the iron group, iron, cobalt and nickel and alloys having one or several of these metals as the predominant ingredient. These metals and alloys will be generally referred to hereinafter as "iron-type metals." The invention has been found particularly advantageous for the coating of nickel-containing stainless steels.

The coated alloys or articles of this invention are primarily intended for use in devices or equipment that are exposed to high temperatures; one of the most important applications is as structural material of aircraft engines which are operated by neutronic reactors.

Stainless steels, in particular chromium- and nickel-containing stainless steels are excellently suitable for neutronic reactors because of their high mechanical strength and their low thermal-neutron-capture cross section; however, at the temperature of, for example, 1038° C. occurring in neutronic reactors, the corrosion resistance of stainless steels is not entirely satisfactory.

It is an object of this invention to provide iron-type metals, in particular stainless steels, with a coating which adequately protects the metal when heated in air at temperatures as high as about 1038° C.

It is another object of this invention to provide a coating on iron-type metals which is resistant to reduction or other chemical attack by said iron-type metals.

It is another object of this invention to provide a coating on iron-type metals which adheres well thereto.

It is still another object of this invention to provide a coating on iron-type metals which has a thermal expansion of similar magnitude to that of the iron-type metal so that a good "fit" is obtained also at elevated temperatures.

It is still another object of this invention to provide a protective coating on iron-type metals which does not spall or flake during thermal shock, that is, during cycling between low temperatures and high temperatures as occurs, for example, in neutronic reactors.

It is finally also an object of this invention to provide a coating on iron-type metals which has a low thermal-neutron-capture cross section.

These objects are accomplished by coating the iron-type metal or article made thereof with a glass composed of from 0.3 to 0.7 mole of alkali metal oxide, from 0.3 to 0.7 mole of strontium oxide, and from 1 to 2.5 moles of silicon oxide. These quantities, expressed in parts by weight, amount to 18.6 to 43.4 parts by weight for sodium oxide, from 8.9 to 20.9 parts by weight for lithium oxide, from 31 to 72.5 parts by weight of strontium oxide and from 60 to 150 parts by weight of silicon oxide.

It was found that a nickel-containing base metal, for instance, when coated with the glass of this invention and "fired" below the melting temperature of the glass and cooled, has a transition zone or interface between base and coating which actually is responsible for the protection obtained against corrosive elements. The inventors do not know with certainty what the chemism is

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which has taken place to form said protective transition zone, but they believe that the nickel of the base alloy diffuses into the glass, possibly in the form of the oxide, whereby a nickel oxide-containing glass interface is formed and a particularly tight and firm bond is obtained. During the service of the coated article and deterioration of the interface layer at high temperatures new portions of nickel probably diffuse into the surface of the coating closest to the base metal and thus continually rebuild an interface whereby the corrosion-resistance of the article is maintained. However, it is emphasized again that this is just a hypothetical explanation for which sufficient proof has not been found.

The composition of the glass should be adjusted so, within the ranges given above, that the glass is sufficiently fluid when melted to make uniform application possible. Both lithium oxide and sodium oxide are especially well suitable alkali metal oxides for the glass of this invention; however, if the coated metal is to be used for neutronic reactors, sodium oxide is preferred on account of its lower thermal-neutron-capture cross section. In some cases the addition of a small quantity of nickel oxide or cobalt oxide to the glass mixture, say between 0.25 and 10% of the batch, is advantageous in order to improve the spalling resistance of the coating.

For the preparation of the glass composition the ingredients were mixed, the alkali and strontium compounds preferably being added in the form of their carbonates. The mixture was then poured into a fire clay crucible, preferably after the latter had been preheated to the melting temperature; the mixture was then melted, which took place between 1230° and 1450° C., the exact temperature, of course, depending upon the composition. After all visible bubbling had ceased, the melt was held at the melting temperature for about another 30 minutes. The glass was cooled in the crucible and then pulverized, e. g. with a steel mortar and pestle, to a mesh size between -200 and -325 or else, the glass, in the melted condition, was poured into cold water whereby it was shattered; in the latter case it was then dried and ball-milled to the proper particle size.

The base metal is advantageously subjected to a pretreatment prior to application of the glass coating. For instance, sand-blasting followed by immersion in boiling carbon tetrachloride for several minutes gave satisfactory results. The metal piece was then dried. In some instances the metal piece was next heated in still air in an electric furnace to about 980° C. for 5 to 10 minutes. The preoxidation step was found advantageous when the coating applied thereafter was fired in an argon atmosphere. When firing was carried out in air, preoxidation was preferably omitted.

The glass can be applied to the base metal by either a dry or a wet method; the latter was preferred because all sides of the surface could be coated in one step. In the dry process powdered glass was shaken through a vibrated sieve onto the surface of the base metal to be coated. The dust-coated metal piece was then fired in an argon atmosphere or in air for from 5 to 10 minutes at between 980° and 1235° C.

For the wet process the glass powder, which had been prepared by pouring the melted mass into cold water, was wet-milled for 1 hour; the mixture best contained from 40 to 70 parts of water per 100 parts by weight of glass powder. In some cases the addition of clay and/or sodium nitrite was advantageous in order to keep the solid particles in suspension. The preferred quantities were about 0.25 part by weight for the sodium nitrite and about 6 parts by weight for the clay. The proportions of the ingredients, it was found, are preferably chosen so that the specific gravity of the water-glass slurry ranges between 1.65 and 1.85, the exact values within this range

depending on the thickness of the coating desired. The pH value of the slurry usually was between 11.2 and 12.0. If the glass was not applied to the base metal immediately after preparation of the slurry, water had to be added during aging in order to maintain the consistency constant at the desired value. The base metal pieces or articles were immersed in the aqueous glass slurry, and the metal, which was coated on all sides, was then dried for about 30 minutes, for instance under an infrared lamp, and finally fired under the same conditions as were the coatings made by the dry process.

The thickness of the coating is not of vital importance because, it was found, as stated before, the interface actually is the protective layer. A coating between 1 and 2 mils thick, after firing, was found to be sufficient.

The coated alloys or articles were tested for adherence and "fit" of the coating, and also for resistance to thermal shock and to oxidation. The adherence was studied by bending a test specimen by about 90° around an iron rod 3" in diameter and investigating the amount of bare metal exposed thereby. The fit, which is dependent on the thermal expansion values of coating and base metal, was considered satisfactory when a 4- to 6-mil thick coating did not spall from the metal or did not cause the base metal to warp during firing.

scopic examination of the interfacial zone between the base metal and the coating.

In the following a number of examples are given which illustrate the properties obtained on stainless steel when coated with the glasses of this invention. Several runs were made with each glass under varied conditions. In all instances the samples were 1" x 1" x 0.016", and the base steel contained about 25% by weight of chromium and about 20% of nickel in all cases except for glass No. 9 where the base steel contained about 23% of chromium and about 14% of nickel. The specimens were sandblasted and cleaned in boiling carbon tetrachloride prior to coating. The glass was then applied by the dry or the wet method. In the case of the dry method only one surface was coated with the glass, while by the wet process all surfaces were coated. The coated specimens were fired for 5 minutes and then cooled. Thereafter they were bent by approximately 90° around a 3/16" diameter rod for testing at about 1040° C.

The coating conditions and test results of the different runs are compiled in the table below. In this table the letter "D" designates that the coating was applied by the dry process and the letter "W" that the wet process was used. Preoxidation, where indicated, was carried out at 982° C. for 8 minutes.

Glass No.	Composition, parts by weight	Coating Method	Preoxidized	Coating fired for 5 minutes		Cycling of Bent Specimen between room temperature and 1040° C. for 112 hrs.	
				In Atmosphere of—	At ° C.	Weight change, mg./in. ²	Appearance
1	18.6 Na ₂ O, 31.7 SrO, 49.7 SiO ₂	D	No	Air	1,120	-32	Dull, spotty, spalled.
		D	No	Air	1,150	-9.5	Spalled, dull.
		D	Yes	Argon	1,150	-2.2	Do.
		D	No	Air	1,038	-15	Dull, distorted.
2	18.7 Na ₂ O, 18.1 SrO, 63.2 SiO ₂	D	No	Air	1,065	-11	Do.
		D	No	Air	1,093	-23	Dull, spotty.
		D	No	Air	1,150	-13	Glossy, spotty.
		D	No	Air	1,204	-7.9	Glossy.
3	26.9 Na ₂ O, 21.5 SrO, 51.6 SiO ₂	D	Yes	Argon	1,065	-11	Do.
		D	No	Air	1,010	-10	Dull, distorted.
		D	Yes	Argon	1,010	-3.6	Do.
		D	Yes	Air	1,010	-2.7	Do.
4	26.9 Na ₂ O, 21.5 SrO, 51.6 SiO ₂ , 6 Clay	W	No	Air	1,010	-4.8	Glossy.
		W	Yes	Argon	1,010	-24	Glossy, spotty.
		W	No	Air	1,010	-5.2	Glossy.
		W	Yes	Argon	1,010	+4.4	Dull, spotty.
5	26.6 Na ₂ O, 21.3 SrO, 51.1 SiO ₂	D	Yes	Air	1,010	+0.9	Do.
		D	No	Air	982	-0.1	Dull, distorted.
		D	Yes	Argon	982	-5.5	Do.
		D	Yes	Air	982	+13	Do.
6	26.6 Na ₂ O, 21.3 SrO, 51.1 SiO ₂ , 6 Clay	W	No	Air	982	-30	Glossy, spotty.
		W	Yes	Argon	982	-42	Dull, spotty.
		W	No	Air	982	-18	Glossy, spotty.
		W	No	Air	982	-63	Do.
7	20.0 Na ₂ O, 36.0 SrO, 44.0 SiO ₂	W	Yes	Argon	982	-59	Dull, distorted.
		W	Yes	Air	982	-53	Dull, spotty.
		D	No	Air	1,232	-11	Spalled, dull.
		D	Yes	Argon	1,232	-5.3	Dull, spotty.
8	20.0 Na ₂ O, 36.0 SrO, 44.0 SiO ₂ , 6 Clay	D	Yes	Air	1,232	-15	Spalled, dull.
		W	No	Air	1,232	-30	Dull, spotty.
		W	Yes	Argon	1,232	-17	Do.
		W	Yes	Air	1,232	-32	Do.
9	5 Li ₂ O, 30 SrO, 65 SiO ₂ , 5 Co ₂ O ₄	W	No	Air	1,232	-68	Do.
		W	Yes	Argon	1,232	-13	Spalled, dull.
		W	Yes	Air	1,232	-33	Do.
		D	No	Air	1,038 for 15'	Not determined.	Good, no spalling.

Resistance to thermal shock was determined by cycling a coated test specimen between room temperature (about 25° C.) and 1040° C. For this purpose the specimen was bent by about 90° around a rod 3/16 of an inch in diameter. The bent specimen was placed on an alumina brick and heated in a furnace at about 1040° C. for 8 hours; it was then removed from the furnace and cooled quickly in air of room temperature. After 1 hour the specimen was returned to the furnace and the cycle was repeated. This thermocycling was carried out until failure or for a maximum test period of 112 hours.

Spalling was determined by visual examination with the unaided eye and also with a low-powered microscope. The effect of thermocycling on the oxidation, too, was studied by visual examination, but also by determining the change of weight of the specimen and by micro-

All the glasses used had a comparatively low thermal-neutron-capture cross section. The maximum cross section per atom was 4.5 barns and the average cross section per atom was about 0.5 barn.

The various runs in the table and in particular those made with glass No. 1 and glass No. 7 show that, in order to obtain good protection, the silica content of the glass has to be at least 1 mole when only 0.3 mole each of sodium oxide and strontium oxide are used. The runs made with glass No. 2, for instance, illustrate that firing in argon gas is not superior to firing in an atmosphere of air, and the runs made with glass No. 3 indicate that firing in air is even better. The examples furthermore show that, for best results, firing should either be carried out in air when the base metal had not been preoxidized, or, when using a preoxidized base metal, an

argon atmosphere should be used during firing. The runs carried out with glass No. 5 demonstrate that, as to appearance, the wet method for applying the glass coatings yields better results than the dry method. However, the weight change which, of course, indicated the total change on all sides whether coated or not, was higher on the samples coated by the dry method although then only one side was coated.

The runs carried out with glass No. 5 and those made with glass No. 4 together indicate that the firing temperature of 1010° C. is better than that of 982° C. The runs with glass No. 6, probably also because of the low firing temperature of 982° C., did not yield too satisfactory results.

The adherence of the glass was satisfactory in most instances. As to cold-adherence and continuity of the coating, glasses No. 1 and No. 3 yielded the best results. Microscopic examination after firing showed that the interface had a ragged contour and contained metallic particles, which indicated that a reaction had taken place between the stainless steel and the glass. The more pronounced these phenomena were, the better was the bond and adherence between coating and base metal. After thermal cycling a continuous nonmetallic phase was noticed in the coating near the interface.

The same steel as used as base metal for the coated test specimens scaled very badly when subjected to thermal cycling under the test conditions.

It will be understood that this invention is not to be limited by the details given herein but that it is susceptible to changes within the scope of the appended claims.

What is claimed is:

1. A structural material consisting of a base of metal the predominant amount of which is metal selected from the group consisting of iron, cobalt, nickel, and any mixtures thereof and a coating of glass firmly bonded thereto, said glass consisting of from 0.3 to 0.7 mole of an alkali metal oxide, from 0.3 to 0.7 mole of strontium oxide, and from 1 to 2.5 moles of silicon oxide.

2. The material of claim 1 in which the base metal is a stainless steel.

3. The material of claim 2 in which the stainless steel contains from 24 to 26% by weight of chromium and from 19 to 22% by weight of nickel.

4. The material of claim 1 in which the alkali metal oxide is lithium oxide.

5. The material of claim 1 in which the alkali metal oxide is sodium oxide.

6. A method of preparing a novel structural material consisting of applying a powdered mixture of from 0.3 to 0.7 mole of alkali metal oxide, from 0.3 to 0.7 mole of strontium oxide and from 1 to 2.5 moles of silicon oxide to the surface of a base of a metal the predominant amount of which is metal selected from the group consisting of iron, cobalt, nickel, and any mixtures thereof, and firing the thus-coated base for from 5 to 10 minutes at a temperature of between 980° and 1235° C.

7. The process of claim 6 wherein the base is heated in air at about 980° C. prior to applying the glass powder and firing is carried out in an atmosphere of argon.

8. A method of making a nickel-containing stainless steel heat-resistant and suitable for use in neutronic reactors consisting of pouring a melted glass mixture of from 0.3 to 0.7 mole of sodium oxide, from 0.3 to 0.7 mole of strontium oxide and from 1 to 2.5 moles of silicon oxide into cold water to form a slurry of a specific gravity between 1.65 and 1.85; immersing the stainless steel into the slurry whereby it is coated with said slurry; drying the coated steel and firing it for from 5 to 10 minutes at a temperature of between 980° and 1235° C.

9. The process of claim 8 wherein the steel is heated in air to about 980° C. prior to applying the glass slurry and firing is carried out in an atmosphere of argon.

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