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ALLOY PROCESS

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This invention relates to iron-chromium alloys, especially stainless steels, and to the art of producing the same.

One object of my invention is the provision of a process for producing nitrogen-containing iron-chromium alloys which is simple to perform, requiring little time and labor, and which makes use of an inexpensive and available nitrogen-bearing material.

Another object is to provide a process for producing nitrogen-containing stainless steel, which is economically practiced, which is highly effective in character, which can be employed using a clean and inexpensive nitrogen-containing material which keeps well and is conveniently and easily stored and which is easy to use in conjunction with operations now employed in producing stainless steel.

A further object of my invention is that of providing a process for introducing nitrogen into stainless steel; the employment of which enables the production in a simple, direct manner of stainless steel of fine even grain which is clean, sound, strong, durable, heat-resistant and corrosion-resistant; which possesses high tensile strength, and high impact value; that lends itself to hot and cold working, hardening, polishing, and the like; and which is highly resistant to decarburization and grain growth under the many conditions of fabrication and use.

Other objects in part will be obvious and in part pointed out hereinafter.

The invention, accordingly consists in the combination of elements, composition of ingredients, and mixture of materials, and in the several steps and in the relation of each of the same to one or more of the others as described herein, the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of my invention, it may be noted at this point that stainless steel is a low-carbon alloy of iron and chromium, which usually contains some 10% to 35% chromium, with or without nickel; and for special purposes supplementary additions of manganese, copper, silicon, tungsten, molybdenum, vanadium, titanium, columbium, tellurium, selenium, sulphur, phosphorus and the like. Nitrogen-containing stainless steel possesses many improved characteristics as compared with ordinary stainless steel. The effect of nitrogen upon stainless steel differs depending upon the grade of the steel. For example, Patent No. 2,118,693 to Arness, issued May 24, 1938, discloses nitrogen-treated stainless steel of the ferritic iron chromium grade comprising 10% to 30% chromium, 0.06% to 0.30% carbon and 0.06% to 0.20% nitrogen. Nitrogen, here, lends refinement to the metal grain structure and makes the metal more resistant to decarburization and grain growth in fabrication and use. Such alloy products are more ductile, more workable, and lend themselves more readily to hardening by heat treatment over a wider range of chromium content. The products are of materially improved tensile strength, and cold forming operations can be carried out upon them over a wider range of temperatures.

A nitrogen-containing austenitic-iron chromium nickel alloy is disclosed in the Arness Patent 2,121,391, issued June 21, 1938. Nitrogen improves the work hardening characteristics of a stainless steel of the austenitic grade. Cold worked products formed from such steel are much superior, in elastic limit and in ductility, to ordinary austenitic-iron chromium nickel steel products.

The properties conveyed by the nitrogen content of non-corrosive ferrous alloys are in some respects similar to the well known properties resulting from the use of a small increased amount of carbon without, however, the accompanying undesirable effects of carbon on corrosion resistance and without decarburization and surface grain growth. A particular added amount of nitrogen must be present in stainless steel to lend improvement to certain qualities of the steel. Ordinarily a bath of stainless steel absorbs up to 0.03% nitrogen from the surrounding atmosphere. Usually a nitrogen-containing material is added to the bath in such quantities that the finished metal analyzes some 0.06% to 0.20% nitrogen. Care must be exercised to avoid the absorption of too much nitrogen, otherwise the metal will be defective, unsound and brittle.

Prior processes for introducing nitrogen into non-corrosive ferrous alloys have proven to be expensive in practice or, in other respects, not completely satisfactory. The nitrogen-containing treating materials employed in these processes are, for example, expensive or difficult to procure, or costly to prepare. Moreover, such materials often are difficult to handle without great waste, while others contain certain impurities which affect the metal detrimentally. Still other nitrogen-containing materials are objectionable for, following their use, traces of certain elements inconsistent with particular alloy specifications will be found in the metal. Often it is difficult to control the amount of nitrogen absorbed by a stainless steel bath because of the

nature of the nitrogen-containing material. This is particularly true where a gas high in nitrogen is used to supply the needed quantity of nitrogen. Again, many nitrogen-containing materials fail to yield a sufficient amount of nitrogen unless such materials are used in large quantities. There are, therefore, many important points to be considered when a nitrogen-containing material is chosen for use in introducing nitrogen into stainless steel.

Accordingly, an object of my invention is the provision of a new process and material for introducing nitrogen into non-corrosive ferrous alloys, which enables the cheap production of nitrogen-containing stainless steel, which gives a metal product uniformly containing the proper amount of nitrogen, which enables nitrogen to be introduced into a non-corrosive alloy without the addition of carbon in excessive amounts or of any other objectionable impurity or material which is inconsistent with the alloy metal specifications, and which in use causes a high percentage of available nitrogen to be released into the alloy metal with highly effective and beneficial results.

Referrring now more particularly to the practice of my invention, I introduce nitrogen into a non-corrosive ferrous alloy during its production by way of ferrous ferricyanide $Fe_3(Fe(CN)_6)_2$, more commonly identified by the trade name, Prussian Blue or Turnbull's Blue. Ferrous ferricyanide comprises a plentiful amount of nitrogen. This nitrogen is released readily when the nitrogen-containing material is brought in contact with a bath of stainless steel. In its pure state, ferrous ferricyanide contains about 28% nitrogen, the balance being carbon and metallic iron. The composition of commercial ferrous ferricyanide does not differ considerably from the composition of the compound in its pure state.

I find that around 50% of the nitrogen available in my nitrogen-containing material is picked up by a stainless steel bath. Therefore, since ferrous ferricyanide so effectively lends nitrogen to a metal bath, only small amounts of the material need to be used to accomplish good results. Further, once the amount of nitrogen which is to be introduced into a metal bath is known, it is but a simple matter to place sufficient quantities of ferrous ferricyanide in the molten metal to release the determined amount of nitrogen. The amount of nitrogen which ferrous ferricyanide yields to a particular grade of stainless steel can be ascertained by experiment. Thereafter, the amount of the nitrogen-containing material needed to impart a certain quantity of nitrogen to that particular stainless steel can be based upon previously recorded experimental data.

Ferrous ferricyanide is available commercially in large quantities and at relatively low cost by comparison with heretofore used nitrogen-containing materials.

Dried ferrous ferricyanide, as purchased on the market, is an almost impalpable powder. Thus, when the powdered material is placed on the surface of a stainless steel bath, difficulty is encountered in getting the powder to sink into and mix with the metal. Accordingly, I prefer to increase the density of the material in any convenient and practical manner causing it to sink, mix and give off nitrogen more readily in a bath of stainless steel. For example, I prefer to briquette the ferrous ferricyanide by any well known method, such as by compressing it, using some suitable bonding material, with or without the addition of a weighting material such as steel turnings or filings. I find that my nitrogen-containing material can be mixed and compressed with any solid material that is added to a stainless steel bath during the processing of the steel. As an example, I mix and compress together quantities of ferrous ferricyanide, pulverized low-carbon ferrochrome and a suitable bonding material. As more specifically set out hereinafter, the chrominum and nitrogen contents of a stainless steel bath are increased when my mixture of ferrochrome and ferrous ferricyanide is added to the metal.

As illustrative of the practice of my invention, a heat of stainless steel is produced in any well known manner, for example, by using stainless steel scrap and high-carbon ferrochrome as sources of chromium, as disclosed in Patent No. 1,925,182 to Feild, issued September 5, 1933; or in accordance with the method described and claimed in the Arness Patent No. 1,954,400, issued April 10, 1934, wherein rustless iron scrap and chromium ore are used as the principal sources of chromium; or in accordance with the method described and claimed in the Arness Patent No. 2,056,162, issued October 6, 1936, wherein rustless iron scrap, high-carbon ferrochrome and chrome ore are used.

I make up a finishing slag on the metal bath, employing such materials as ferro-silicon and ferro-manganese. As desired, along with ferro-silicon and ferro-manganese, ferrochrome is added in amounts sufficient to adjust the chromium content of the bath. I also add a proper quantity of briquettes containing ferrous ferricyanide to the metal bath which are decomposed therein. Nitrogen is released by the decomposing briquettes, the nitrogen being quickly assimilated throughout the metal and being absorbed quite readily by the metal. Thereafter, I tap the metal into a ladle from which it is teemed into suitable ingot molds where it is permitted to solidify and cool. The molds are then stripped from the ingots and the ingots stored and converted into various semi-finished products as desired.

Instead of adding ferrous ferricyanide briquettes of the type described above to the metal bath, I obtain very good nitrogen-containing stainless steel by using briquettes comprising a mixture of pulverized low-carbon ferrochrome and ferrous ferricyanide. The chromium and nitrogen present in the bath are brought up to specifications by dropping a sufficient number of these briquettes into the bath during the finishing operation. It is well known that chromium has a great thirst for nitrogen. Much of the nitrogen released by ferrous ferricyanide in the briquettes, as they decompose in the bath, is absorbed immediately by the chromium derived from the ferrochrome briquette constituent. Nitrogen absorption, therefore, is very complete since the nitrogen is in immediate contact with an abundance of chromium. The added chromium, and the nitrogen which it absorbs, are distributed uniformly throughout the metal bath during the processing operation. As before, the finished metal is tapped into a ladle and teemed into ingot molds to solidify and cool.

At times, I find it advantageous to introduce ferrous ferricyanide into stainless steel before the furnace finishing stage is reached, or during, or after the tapping of the melt into a ladle following the furnace finishing stage. Generally, the

amount of carbon which the metal picks up from ferrous ferricyanide is not objectionable. When, however, the production of extremely low carbon, nitrogen-containing stainless steel is sought, the ferrous ferricyanide is introduced during early furnacing stages and much of the carbon is eliminated from the melt before the finishing stage is reached. Further, I find that an excellent distribution of nitrogen throughout the metal is obtained when my nitrogen-containing material is added to the molten metal in the ladle. This is done by shoveling a quantity of powdered or briquetted ferrous ferricyanide into the ladle during the metal tapping operation. The turbulent action of the metal, as it pours into the ladle, effects a stirring action. This action is highly effective in distributing nitrogen given off by the nitrogen-containing material very completely throughout the metal.

A 13-ton heat of 17% chromium grade stainless steel picks up about 50% of the nitrogen available in ferrous ferricyanide. When the metal analyzes 0.03% nitrogen, approximately 55 pounds of the nitrogen-containing material are required to increase the amount of nitrogen in the melt to 0.06%. Thus, ferrous ferricyanide is highly effective in use. It is very economical to employ for it is cheap to procure and can be used in small quantities with good results.

While my invention is directed praticularly to using ferrous ferricyanide as a nitrogen-introducing material in the production of stainless steel, nitrogen also may be introduced into ferrochrome during its production, this preferably being added to the melt during the reducing period. Also, in the production of stainless steel. There are other alternative materials which I propose to use in lieu of ferrous ferricyanide. Copper cyanide, for example, can be employed in powdered or briquetted form for introducing nitrogen into a stainless steel which contains copper as an alloying element. Further, the use of other cyanides and ferricyanides of such metals as the alkali metals, particularly sodium and potassium, fall within the scope of the present invention.

Further, the non-corrosive ferrous alloys upon which my invention is practiced, in consequence, are much improved in quality. A uniform distribution of nitrogen is obtained throughout the metal. The nitrogen, therefore, imparts a more uniform and even grain structure and a consistently finer grain structure to the metal. The finished alloy is free from impurities and no trace of metal foreign to the desired elements in the alloy is present. Such metals are strong and durable throughout and are free from gas flaws and other defects.

Thus it will be seen that in the present invention, a new process for introducing nitrogen into stainless steel is provided, by the use of which the various objects hereinbefore noted, along with many thoroughly practical advantages, are successfully achieved. It will be observed that the physical properties of rustless ferrous alloys are greatly improved by the practice of my invention and that these improvements are achieved at great savings in manufacture heretofore unrealized; and that the useful field of application of these products has been broadened both from the standpoints of economy and improved quality.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments hereinbefore set forth, it is to be understood that all matter described herein is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. In the production of iron-chromium alloys of appreciable nitrogen contents, the art of which includes preparing in a suitable furnace a bath of ferrous metal containing chromium and adding to said metal bath a quantity of briquetted nitrogen-containing material comprising substantial amounts of ferrous ferricyanide and low carbon ferrochrome.

2. In manufactures of the class described, a briquetted nitrogen-treating agent comprising a substantial amount of ferrous ferricyanide and ferro-chromium.

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