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ALLOY PROCESS

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This invention relates to stainless steels and more particularly to an art of producing the same.

Among the objects of my invention is the provision of a process having great utility in the production of stainless steels containing columbium, which permits the introduction of columbium into stainless steel in a simple, direct and economical manner, giving a lustrous, workable, corrosion-resistant product, which enables the production of stainless steel possessing high resistance to intergranular corrosion and embrittlement.

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

The invention accordingly consists in the combination of elements, composition of ingredients, and in the several steps and 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 certain aspects of my invention, it may be noted at this point that stainless steel is defined as a low-carbon steel comprising 10% to 35% chromium, with or without nickel and supplemental additions of such elements as manganese, silicon, copper, tungsten, vanadium, molybdenum, titanium, columbium, sulphur, phosphorous, selenium, tellurium, and the like for special purposes, and the balance substantially all iron.

Among the stainless steels to which my invention most particularly relates, are the austenitic steels. These steels are defined as steels comprising 7% to 15% nickel, 10% to 35% chromium, with or without the supplemental additions noted for special purposes, and the balance substantially all iron.

The austenitic stainless steels are not found to be especially adapted for duty under strongly oxidizing or corrosive conditions, or conditions involving appreciable working stresses following a heating within a certain critical temperature range of some 500-900° C., largely because of the susceptibility of these steels to intergranular corrosion. Moreover, while these steels are welded quite readily, much difficulty is encountered in that intergranular corrosion develops adjacent to the welded sections of the metal.

The phenomenon of intergranular corrosion of metals has been explained by the formation and precipitation of carbides at the grain boundaries leaving the metal susceptible to attack at these boundaries. When austenitic stainless steels are heated, carbon comes out of solid solution. Car-

bide particles accumulate at the metal grain boundaries, apparently obtaining most of the chromium from the surface of the grains. Decreased amounts of chromium near the surface of the metal grains make these metal grains less resistant to corrosion. As long as carbide particles are dispersed throughout the grains, the possibility of intergranular corrosion is negligible, but when strong chromium carbide particles precipitate to the grain boundaries, corrosion will take place and the metal often is no longer suitable for service. Moreover, intergranular corrosion causes the metal to become embrittled and weak and the utility of the metal accordingly is impaired still further.

The problem of preventing intergranular chromium carbide formation in austenitic stainless steels has been dealt with by introducing certain alloying elements into the steel. For example, such metals as titanium and columbium have been used for this purpose with good results. These metals are very strong carbide formers and they, therefore, prevent the precipitated carbon from becoming available to combine with chromium as mentioned hereinbefore. Chromium dispersion remains substantially the same throughout the alloy with the results that little or no corrosive action takes place.

Methods heretofore employed in introducing columbium into stainless steel are expensive, indirect or otherwise unsatisfactory. For example, a prealloy of ferro-columbium has been much used in the manufacture of columbium-containing steel, but this prealloy has certain properties making it undesirable for use as a material to be introduced into steel baths. Because of the high melting point of ferro-columbium, it is difficult to dissolve the prealloy in a steel bath rapidly and without considerable oxidation of the columbium. Moreover, prealloys of low-carbon content are costly to prepare or to procure. Introducing an alloying element into a metal bath through the medium of a prealloy is a more indirect operation than if the elements were reduced directly from its ore.

The need for a more simple, direct and economical process for producing columbium-containing stainless steels has been recognized for quite some time. The direct use, in the furnace, of ores comprising substantial amounts of columbium, heretofore has been given consideration. Because of poorly directed experiments, such practice was deemed to be impractical. Colum-
bium yield from the ore proved to be much too low for commercial purposes.

Accordingly, an object of my invention is to provide a practical process for introducing columbium into stainless steels by the direct use of columbium-containing ore, which process is adapted for practice during the finishing stages undergone by the metal bath, which enables a high percentage of columbium in the ore to exchange from the ore to the metal bath, which is practiced without encountering excessive amounts of slag, and which permits the production of a finished alloy having high corrosion resistance; particularly with respect to intergranular corrosion.

Referring now, more particularly to the practice of my invention, I introduce columbium ore together with a suitable reducing agent into a bath of stainless steel as a part of the steel finishing operation. I find that columbite, which contains substantial amounts of columbium oxide, is a satisfactory source of columbium. The columbium ore preferably is crushed, and then it is mixed with a certain quantity of metallic reducing material such as calcium, calcium-silicon, silicon, aluminum, ferrosilicon, or ferroaluminum. The mixture of crushed ore and reducing material is changed into a bath of stainless steel.

Ordinarily the bath of stainless steel of desired analysis is first prepared and any slag is removed. Then a finishing slag of lime and fluorspar is prepared on the surface of the metal. The columbite and reducing agent are added to the finishing slag overlying the alloy metal bath. Columbium reduced from the ore goes into the bath quite readily. The gangue from the ore and the silicon or alumina resulting from the reduction remain in the slag. The bath of metal, now containing a desired amount of columbium, is tapped into a ladle and from the ladle is teemed into a mold to solidify and cool. The resultant ingots are converted through known methods into plate, sheet, strip, bars, rod, wire, tubes and the like which subsequently are fabricated, as by welding, into a host of articles of ultimate use.

As illustrative of the practice of my invention, I produce a 13-ton heat of austenitic grade of chromium-nickel stainless steel in a suitable furnace; for example, by melting stainless steel scrap and high-carbon ferrochrome under strongly oxidizing conditions as, wherein carbon is eliminated and chromium is oxidized and the oxide migrates to the slag, and then reducing the chromic oxides in the slag as described in Patent No. 1,925,182 to Feild, issued September 5, 1933. The heat of metal also may be produced in accordance with the method disclosed in the Arness Patent No. 1,954,400, issued April 10, 1934, wherein similar oxidation and reduction periods are used and wherein rustless iron scrap and chromium ore are employed as principal sources of chromium; or in accordance with the similar method described and claimed in the Arness Patent No. 2,056,162, issued October 6, 1936, wherein rustless iron scrap, chrome ore and high-carbon ferrochrome are used. The nickel addition is made during the melting period conveniently as electrolytic nickel.

Following the reduction of the heat of metal, I remove the slag formed on the surface of the metal bath. A carbon analysis is quickly made. A finishing slag preferably is prepared on the surface of the reduced bath by scattering lime and fluorspar over the bath surface.

I then introduce a mixture comprising pulverized columbite and ferrosilicon into the bath

of austenitic steel. For a 13-ton heat having a carbon content of .10% and available columbite analyzing 60% Cb_2O_5 , 775 pounds of columbite and 155 pounds of contained silicon are employed to give a columbium to carbon ratio of 10 to 1. Columbium in the bath is reduced to columbium by the silicon, the metallic columbium going into the steel and the formed silica remaining in the slag. The metal is tapped from the furnace into a ladle for teeming into ingot molds and where it is permitted to solidify and cool. The finished ingots contain about 1.0% columbium and less than 1% silicon.

The quantity of columbium going into the metal bath should be so controlled that there is sufficient columbium available to combine with the carbon content of the metal. On the other hand, an excessive amount of columbium should not be introduced, for if this is done, workability of the metal will be affected detrimentally. Austenitic steels in which the columbium-to-carbon ratio is approximately 10 to 1 possess high resistance to intergranular corrosion together with good workability.

The amount of reducing agent which I mix with columbium ore is governed by the quantity thereof needed to effect reduction of the ore. Excess amounts of the reducing agent are generally used. I find that the ratio of columbite ore to aluminum or silicon, for example, should be approximately 3 to 1. The recovery is approximately 80 percent.

Austenitic stainless steels finished in accordance with my invention usually comprise 7% to 15% nickel, 10% to 35% chromium, 0.03% to 0.12% carbon, 0.3% to 1.2% columbium, less than 1% silicon or aluminum with or without supplemental amounts of one or more of such elements as manganese, copper, tungsten, molybdenum, titanium, vanadium, sulphur, phosphorus, selenium, tellurium, and the like, for special purposes, and the balance substantially all iron.

The materials employed in my process are cheap and readily available. My process is adapted to form a part of conventional metal finishing operations and requires little or no altering or shifting of metallurgical equipment usually employed in the production of stainless steel. The process is direct, since raw materials are introduced directly as a part of the metal finishing procedure. I find that the stainless steels readily take up the columbium content of the columbite ore. Only small waste of raw materials, therefore, is involved in the practice of my process. Finished alloy products are obtained in a simple, inexpensive manner; these products being clean, strong, and durable.

Although the application of my process to the production of austenitic grade stainless steels has been stressed hereinbefore, it is to be understood quite clearly that the process is suitable for other applications. For example, my process may be employed in alloying columbium with stainless steels of the ferritic grade, the only change in the steps hereinbefore noted being that columbite ore is introduced into a bath of stainless steel of ferritic quality rather than of the austenitic grade.

I find that when ore containing an oxide of columbium is introduced in pulverized form into a bath of stainless steel, the ore yields a good amount of columbium to the bath. Metallic reducing agents such as calcium, calcium-silicon, silicon, aluminum, ferrosilicon or ferroaluminum, or combinations thereof, are added to the steel

bath either in admixture with the columbium ore or separately from the columbium ore.

Thus it will be seen that in the present invention, a new process for introducing columbium into stainless steels is provided, by the use of which the various objects hereinbefore noted, along with many thoroughly practical advantages, are successfully achieved. It will be seen that the products made in accordance with this process are clean, strong, workable and highly resistant to corrosion, particularly to intergranular corrosion, and that these characteristics are achieved at great savings in manufacture heretofore unrealized; and that the field of application of these products has been broadened from the standpoint of economy without sacrificing quality.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiment 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.

What I claim is:

1. In the production of stainless steel of appreciable columbium contents, the art which includes preparing in a suitable furnace a bath of ferrous metal containing chromium in substantially the amount desired in the finished steel, preparing a limy finishing slag overlying the bath, and introducing into the slag a quantity of columbium ore and a silicon reducing agent as a metal finishing step.

2. In the production of stainless steel alloys of appreciable columbium contents, the art which includes preparing in a suitable furnace a bath of austenitic grade ferrous metal comprising

substantial amounts of chromium and nickel, and introducing into the bath in the presence of a limy finishing slag a quantity of columbium oxide and a ferro-silicon reducing agent as a metal finishing step.

3. In the production of stainless steel alloys of appreciable columbium contents, the art which includes preparing in a suitable furnace a low-carbon bath of ferrous metal containing chromium and nickel in substantially the amounts desired in the finished steel, introducing columbium into the bath as a finishing step by addition to the bath of lime and a mixture comprising substantially three parts columbite and one part silicon-containing reducing agent, the ratio between the columbium introduced and the carbon in said bath being substantially 10 to 1.

4. In the production of stainless steel alloys of appreciable columbium contents, the art which includes preparing in a suitable furnace a bath of austenitic grade ferrous metal comprising 10% to 35% chromium, 7% to 15% nickel, and 0.03% to 0.12% carbon, and introducing into the bath as a metal finishing step lime and a mixture comprising substantially three parts columbite and one part silicon reducing agent.

5. In the production of stainless steel alloys of appreciable columbium contents, the art which includes preparing in a suitable furnace a bath of austenitic grade ferrous metal comprising 10% to 35% chromium, 7% to 15% nickel, and 0.03% to 0.12% carbon, preparing a limy finishing slag on the bath and introducing into the bath as a metal finishing step a mixture comprising columbite and crushed ferro-silicon.

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