

UNITED STATES PATENT OFFICE

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ALLOY PROCESS

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This application is a continuation in part of my copending application, Serial Number 396,913, filed June 6, 1941, entitled Alloy process, now Patent 2,336,237 of December 7, 1943, and the 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 clean, sound, 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 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, phosphorus, 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

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boundaries. When austenitic stainless steels are heated, carbon comes out of solid solution. Carbide 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 less direct than if the element 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 producing a columbium-bearing stainless steel by the direct use of columbium-containing ore, which process is adapted for practice using conventional melting equipment which enables a high recovery of columbium in the ore and yet which gives a finished alloy which is clean and sound having high corrosion resistance, particularly with respect to intergranular corrosion.

Referring now more particularly to the practice of my invention, a bath of stainless steel of desired chromium analysis first is prepared. Adjustments of analysis and additions of supplementing agents are made. The metal then is tapped into a ladle for teeming.

During the tapping operation, columbium ore such as columbite, together with a suitable reducing agent, is added to the ladle. Preferably the columbium ore is preheated prior to use. Moreover, the preheated ore preferably is added to the ladle with finely crushed ferrosilicon. In general, the ferrosilicon is used in about 25% excess over the theoretical requirement. In addition, the ore and ferrosilicon preferably are charged into the ladle early in the tap and moreover, the ladle is rabbled as the tapping progresses.

Columbium reduced from the ore goes into the bath quite readily. The reaction is aided by the turbulence of the metal poured into the ladle, the gangue from the ore and the silicon resulting from the reduction remain in the ladle. The bath of metal, now containing a desired amount of columbium, is teemed into molds 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 the metal, it is tapped into a ladle. During the initial stages of tapping, I introduce a mixture of columbite and ferrosilicon previously conveniently mixed up on the floor of the meltshop.

For a 13-ton heat having a carbon content of .07% and available columbite analyzing 60% Cb_2O_5 , 475 pounds of columbite and 150 pounds of contained silicon are employed to give a columbium to carbon ratio of 10 to 1. Columbite 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 .80% columbium and less than 0.75% 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 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 10% to 35% chromium, 7% to 15% nickel, 0.03% to 0.10% carbon, 0.3% to 1.0% columbium, less than 1% silicon 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.

One of the most popular grades of columbium-bearing stainless steel made in accordance with my invention analyzes, 17.50 to 19.00% chromium, 10.50 to 14.00% nickel, 1.25 to 2.00% manganese, .07% carbon maximum, columbium eight times the carbon as a minimum and 1% as a maximum, .35 to .75% silicon, and iron the remainder.

The materials employed in my process are cheap and readily available. The process is direct, since raw materials are introduced directly into the ladle. 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. The columbium recovery is consistently high and the columbium content may be made to reasonably close tolerances. 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 stainless steel has been illustrated 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 martensitic and ferritic grades.

Thus it will be seen that there is provided in the present invention, a new process for producing a columbium-bearing stainless steel, 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 process is simple and direct and moreover that it is thoroughly practical and reliable.

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

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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 content, the art which includes preparing in a suitable furnace a bath of ferrous metal containing the required chromium content, tapping the bath into a ladle, and during the tapping operation making said columbium addition by charging into the ladle columbium ore and a reducing agent.

2. In the production of stainless steel of appreciable columbium content, the art which includes preparing in a suitable furnace a bath of stainless steel, tapping the bath of steel into a ladle, and during the initial stages of the tapping operation making said columbium addition by charging into the ladle a mixture of columbium ore and crushed ferrosilicon.

3. In the production of stainless steel of appreciable columbium content, the art which includes preparing in a suitable furnace a bath of stainless steel, tapping the bath of steel into a ladle, and during the tapping operation making said columbium addition by charging into the ladle columbium ore and a silicon reducing agent, the amount of reducing agent being chemically in excess up to about 25% of that required by the columbium ore.

4. In the production of austenitic chromium-nickel stainless steel of appreciable columbium content, the art which includes preparing a bath of chromium-nickel austenitic stainless steel, tapping said bath into a ladle, and during the

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tapping operation making said columbium addition by charging into the ladle a mixture of about three parts columbite and one part silicon reducing agent.

5. In the production of austenitic chromium-nickel stainless steel of appreciable columbium content, the art which includes preparing a bath of austenitic chromium-nickel stainless steel, tapping said bath into a ladle, and during the initial stages of the tapping operation making said columbium addition by charging into the tapped metal a mixture of preheated columbite and crushed ferrosilicon.

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