United States Patent Office 2,839,391 Patented June 17, 1958

2,839,391

CHROMIUM-MANGANESE ALLOY AND PRODUCTS

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No Drawing. Application October 21, 1954 Serial No. 463,800

9 Claims. (Cl. 75—126)

This application for patent is a companion to my application Serial No. 357,890, entitled Melting Process and Product, and filed May 27, 1953, now Patent No. 2,750,283, issued June 12, 1956, as a continuation-in-part of my application Serial No. 238,593, filed July 25, 1951, now abandoned, and the present invention relates to high alloy steels of satisfactory hot-working qualities and to various articles fashioned thereof.

Among the objects of my invention is the provision of highly alloyed steels, especially austenitic chromium-manganese stainless steels and austenitic chromium-manganese-nickel stainless steels, of great strength and hardness at high temperatures and yet possessing good ductility at high temperatures and good hot-working properties to give billets, bars and other converted products of good surface which are free of checks and tears, all with a minimum of reheating in the conversion from ingot to billet and from billet to bar and with a minimum of grinding or other surface finishing.

Another object is the provision of austenitic chromium-manganese steel plates, sheets, bars, rods, wire and like converted products of good surface at minimum expense in conversion and with high recovery with a minimum of handling.

A further object of my invention is the provision of austenitic chromium-manganese steel bar stock that readily lends itself to hot-extrusion to form internal combustion engine valves and to wire stock that readily may be upset to form internal combustion engine valves.

Other objects of my invention in part will be obvious and in part pointed out during the course of the following description.

My invention accordingly relates to the combination of elements, composition of ingredients and mixture of materials, and to the useful articles of manufacture fashioned of the same as described herein and as set forth in the claims at the end of this specification.

As conducive to a better understanding of certain features of my invention it may be noted at this point that the highly alloyed chromium-manganese steels, especially the austenitic chromium-manganese and chromium-manganese-nickel stainless steels possess many desirable physical characteristics. These are strong and hard at high temperatures. And various articles manufactured of these steels possess long useful life under high temperature operating conditions in the presence of various active corrosive agents as well as various oxidizing agents.

As may be expected, however, such steels because of their high temperature strength and hardness, qualities

for which they are sought out from the best of alloys on the market, are very difficult to work. They are difficult to hot-roll from ingot to billet and equally difficult to convert from billet into bar, wire and the like. Many reheatings and rehandlings are required in the working and conversion. Great care must be exercised by the rolling mill operator to quickly note any sign of check or tear in the surface of the work in process in order that the partially converted product may be withdrawn from the mill, reheated and then further processed. For otherwise the check or tear will quickly grow. Badly torn metal must be cropped off and scrapped. And to eliminate the imperfections in the less badly checked or torn metal at the conclusion of the rolling operation, there is required excessive grinding or other surface finishing operation with great expenditure of time and with substantial loss of metal. As a result, the hot-working of the highly alloyed chromium-manganese steels is costly and time consuming.

One of the objects of my invention therefore is to provide a chromium-manganese steel of high alloy content such as an austenitic stainless steel which enjoys the great strength and high hardness values of the steels of the prior art, yet which are of substantially improved hot-working qualities with a minimum of handling and reheating the work in the mill and with a maximum of yield in conversion from ingot to billet or other converted product and a minimum of scrap and minimum of expensive finishing operations. A further object is the provision of austenitic chromium-manganese stainless steel bars, rods and wire which readily may be extruded or upset, with minimum loss and scrap, in the production of internal combustion engine exhaust valves.

Considering now more particularly the practice of my invention I find that by incorporating a very small critical amount of boron in the highly alloyed chromium-manganese steels important and highly desirable hot-working benefits are had. For some reason unknown to me the ductility of the steel is markedly improved and yet the desired high temperature properties do not appreciably suffer. While it might be expected that with the increase in hot-ductility there would be a corresponding loss of hot-hardness I find that this is not the case. The metal works well at customary rolling temperatures, yet in use the desired hardness and strength at high temperatures do not suffer.

I find that the boron content of my steel is highly critical. And I employ it only in quantity just sufficient to achieve the desired hot-working characteristics. For with even the slightest excess there is observed an embrittlement of the metal which renders it unfit for use. With but slight excess the metal breaks in rolling and must be scrapped.

My boron addition is made to the steel either in the furnace during the finishing operation, or it is made to the ladle. Good results are had when the addition is made to the ingot mold either before or during teeming. And preferably the boron addition is made in the presence of a deoxidizing agent as appears more fully hereinafter.

As illustrative of the practice of my invention I produce chromium-manganese steel alloys of 12% to 30% chromium, 4% to 20% manganese, up to 1.50% carbon, .00005% to .0050% boron and remainder substantially

all iron. Where desired the alloy also may include nickel up to 35%. Molybdenum may be employed in amounts up to 9%. And cobalt up to 20%. Nitrogen preferably is included, this in amounts from .06% (less than .06% being commonly found in stainless steels, see Jennings U. S. Patent 2,657,130 of October 27, 1953) up to .60% where desired.

In my alloy the amount of boron is especially critical for reasons explained above. Actually I find that the best range of boron is from about .0005% to .0008%. Although the amounts of the other ingredients are not quite so critical any lower chromium content fails to give the desired corrosion resistance and any greater amount is an unnecessary waste. Moreover, it upsets the important structural balance of the steel, thereby requiring excessive additions of other ingredients to restore balance. The manganese is employed to establish the desired austenitic structure, lesser amounts would be insufficient and greater amounts would detract from corrosion resistance.

The carbon content is critical in that greater amounts than 1.5% cause rolling difficulties; i. e. excessive hardness and splitting in rolling. Nitrogen preferably is employed, this in the amount of .06 to .60% as noted, because I find that it contributes to high temperature hardness. Excessive quantities of nitrogen are avoided, however, because they tend to create unsoundness.

Nickel is beneficial in that it helps stabilize the desired austenitic structure of the steel. Cobalt is beneficial in lending high temperature strength.

Sulfur, where added to improve the machining characteristics of the metal, is permitted in amounts only up to .30%. Greater amounts give rise to hot-working difficulties, particularly splitting in the mill.

As a preferred composition my alloy is a fully austenitic stainless steel essentially comprising 18% to 24% chromium, 6% to 12% manganese, .30% to .60% carbon, up to 5% nickel, up to .15% sulfur, .06% to .60% nitrogen, .0001% to .0050% boron and remainder substantially all iron. This steel is hard at high temperatures of use such as 1400° F. and also hard at rolling temperatures. But I find that it possesses sufficient ductility at rolling temperatures to give enhanced rolling characteristics. The ductility does not adversely affect the hardness at 1400° F.

In the production of my chromium-manganese stainless steels I frequently employ the electric arc furnace melting practices of the Feild U. S. Letters Patent 1,925,182 or that of the Arness U. S. Letters Patent 1,954,400.

To the chromium-manganese stainless steel melt I make a boron addition in the form of various boron prealloys such as ferro-boron, silicon-boron, manganese-boron, aluminum-boron either with or without deoxidizing agents such as silicon, titanium, vanadium or zirconium. The addition alternatively may be made by way of boron oxides or dehydrated borates such as boric acid and pyrobor. Conveniently I use rasorite or other naturally occurring borate such as borax.

The boron addition, as indicated above, is made either in the furnace, or the ladle or the ingot mold. Following my usual practice I add the boron-containing substance, illustratively, rasorite, direct to the ladle, preferably along with a strong deoxidizing agent selected, for example, from the group consisting of ferro-titanium, calcium-silicon, aluminum, ferro-silicon, and silicon-manganese-aluminum alloy. These deoxidizers are selected from the group which performs the function of combining with the oxygen in the metal. Other deoxidizers which are satisfactory include aluminum-silicon, chromium-silicon, manganese-silicon, magnesium-silicon, magnesium-manganese-silicon, ferro-zirconium, silicon-zirconium, nickel-zirconium and calcium metal.

In making the preferred additions to the metal, rasorite is in the form of a sand, while the ferro-titanium is in the form of lumps up to about 1½ to 2 inch, and the calcium-silicon is in lumps of about ½ inch to ¾ inch size. These ingredients are added one after the other, it being immaterial which is added first, or they may be mixed and added as briquettes if desired. Preferably it is added to the ladle, but if added to the furnace the addition is poked through the slag with an iron rod. The rasorite and the calcium-silicon melt before reaching the top of the bath. The ferro-titanium, however, sinks into the bath. These ingredients may also be added to the ingot mold.

The ferro-titanium and calcium-silicon are added in the respective amounts of about 4 pounds and 2 pounds per ton of stainless steel to be produced. The amount of rasorite employed ranges from about ½ pound to 2 pounds per ton of steel to be produced, the higher amounts being for the steels of the higher total alloy content.

The furnace is tapped into a ladle for teeming. And the teemed metal is allowed to cool and the molds stripped from the resulting ingots.

For valve steels I usually produce 10" x 10" ingots and hot-roll them to 3" x 3" billets. These are then ground and worked into bars of 1 to 2" diameter.

As illustrative of the practical importance of the markedly improved hot-rolling characteristics of my austenitic chromium-manganese stainless steel I give below certain hot-rolling data for an internal combustion engine valve steel in accordance with my invention (Table I) as compared with that for a like steel, but without boron (Table II). My steel generally is of the composition: 20.00% to 22.00% chromium, 8.00% to 10.00% manganese, 3.25% to 4.50% nickel, .47% to .57% carbon, .38% to .50% nitrogen, up to .10% sulfur, .25% maximum silicon, .0001% to .0050% boron and remainder iron. The comparative steel is the same except for the boron being omitted. The attempt was made in every case to convert the 10" x 10" ingot to a 3" x 3" billet by rolling in a three high fixed pass mill. In most instances my steel was successfully converted to the desired size. In many, however, the work had to be withdrawn from the mill before the desired size was had, this because of evidence of checking. The results had with my steel as compared with steel with boron omitted are given below:

TABLE I

[Hot-rolling results of internal combustion engine valve steel containing boron. Number of ingots converted and extent of reduction permitted.]

Heat	C	Mn	P	S	Si	Cr	Ni	N	B	Ingots to Billets
A	.55	8.35	.012	.072	.17	20.06	3.56	.40	.0006	8 to 3 x 3. 16 to 5½ x 5½.
B	.57	8.32	.015	.063	.15	20.29	3.53	.42	.0005	2 to 7½" sq. (stuck in mill). 24 to 3 x 3.
C	.52	9.25	.013	.060	.16	20.60	3.91	.44	.0006	24 to 3 x 3.
D	.53	8.58	.014	.067	.14	20.49	3.52	.41	.0005	27 to 3 x 3.
E	.50	8.77	.013	.047	.12	20.51	3.41	.41	.0005	1 to 3¾. 29 to 3 x 3.
F	.55	8.30	.012	.062	.18	20.89	3.73	.38	.0008	31 to 3 x 3.
G	.56	8.86	.015	.070	.19	20.50	3.59	.44	.0008	28 to 3 x 3.

TABLE II

[Hot-rolling resulting with the steel of Table I except boron omitted. Number of 10" x 10" ingots converted and amount of reduction permitted.]

Heat	C	Mn	P	S	Si	Cr	Ni	N	Ingots to Billets
K	.53	8.89	.012	.082	.11	20.62	3.69	.42	1 to 4½. 2 to 6 x 6. 20 to 5½ x 5½.
L	.56	8.00	.012	.065	.15	20.75	3.46	.39	24 to 6 x 8. 1 to 5½ sq. 1 to 7½ sq.
M	.56	8.72	.015	.066	.16	20.74	3.51	.43	5 to 7½ sq. 2 to 6 x 8. 17 to 6 x 6.
N	.55	9.09	.013	.050	.14	20.78	3.55	.46	2 to 3 x 3. 2 to 6 x 8. 20 to 5½ sq.
O	.55	8.16	.014	.067	.22	20.97	3.53	.42	3 to 3 x 3. 25 to 5½ sq.
P	.57	9.84	.015	.070	.15	20.53	3.53	.46	2 to 3 x 3. 2 to 4½ sq. 19 to 5½ sq.
Q	.53	8.30	.014	.073	.18	20.75	3.64	.40	13 to 3 x 3. 17 to 5½ sq.
R	.53	8.54	.011	.059	.16	20.75	3.51	.46	2 to 3¾. 27 to 5½ sq.
S	.55	8.69	.013	.077	.17	20.43	3.59	.43	1 to 4½. 7 to 5½. 21 to 6 x 6.
T	.52	9.85	.013	.069	.13	20.61	3.71	.45	1 to 4½. 25 to 5½.
U	.53	8.23	.014	.086	.18	21.03	3.42	.41	1 to 6 x 6. 28 to 7½ sq.

The data presented in Tables I and II above reveals that of the 190 10" x 10" ingots of my invention, in which boron is included, 171 of them successfully rolled into the desired 3" x 3" billet, this representing 90.0% of the ingots converted. Of the 291 10" x 10" ingots of like analysis, but with the boron omitted, only 20 were reduced to the 3" x 3" billet. The others required removal from the mill at various intermediate sizes to permit reheating before further reduction could be undertaken. The number of ingots, there, directly converted to the 3" x 3" size only amounted to 6.9%. The great superiority of my steel in the matter of hot-rollability is thus drastically revealed.

Another specific valve steel according to my invention analyzes about 20.00% to 22.00% chromium, 8.00% to 10.00% manganese, 2.50% to 3.50% nickel, .32% to .42% carbon, .25% to .35% nitrogen, up to .10% sulfur, silicon .25% maximum, .0001% to .0050% boron and remainder iron.

A further specific valve steel is of the composition 20.00% to 22.00% chromium, 8.00% to 10.00% manganese, 3.25% to 4.50% nickel, .55% to .65% carbon, sulfur .03% maximum, silicon .25% maximum, boron .0001% to .0050%, and remainder iron.

Billets according to my invention are reheated and further converted to bars, rods and wire. And I find that these converted products possess the same improved hot-working properties. The bars lend themselves to hot-extrusion in forming internal combustion engine valves, the stem being formed by the extrusion. And rods and wire being readily hot-upset to form valves with upset heads. The internal combustion engine valves are hard, tough and well adapted to withstand long periods of operation at high temperature, 1400° F. and more.

Thus it will be seen that there is provided in my invention an alloy and various converted products and ultimate products of use fashioned of the same in which the various objects hereinbefore set forth are successfully achieved. The steel is strong and hard at high temperatures and yet possesses surprisingly good hot-working characteristics. The steel is converted to billets with a minimum of handling and re-heating. And the converted products have good surface with minimum of check and blemish. Finishing costs are minimized and scrap losses are greatly decreased. As a consequence there are achieved important savings in time, labor and materials. All these, as well as other practical advantages, are had in my invention.

It is apparent from the foregoing that once the broad aspects of my invention are disclosed, many embodiments thereof will readily suggest themselves to those skilled in the art to which my invention relates, all fully within the scope of my disclosure. Accordingly, therefore, I desire my disclosure to be considered solely as illustrative and not by way of limitation.

I claim as my invention:

1. Austenitic alloy steel of improved hot-rolling characteristics essentially comprising 12–30% chromium, 4–20% manganese, up to 35% nickel, up to 1.5% carbon, about .06% to .60% nitrogen. 0.00005 to 0.005% boron, and remainder substantially all iron.

2. Austenitic alloy steel of improved hot-rolling characteristics essentially comprising 12–30% chromium, 4–20% manganese, up to 1.50% carbon, up to 35% nickel, up to 9% molybdenum, up to 20% cobalt, up to .30% sulfur, .06% to .60% nitrogen, 0.00005% to 0.005% boron, and remainder substantially all iron.

3. Hot-rolled austenitic stainless steel bars essentially comprising 12–30% chromium, 4–20% manganese, up to 1.5% carbon, up to 35% nickel, up to 9% molybdenum, up to 20% cobalt, up to .30% sulfur, .06% to .60% nitrogen, 0.00005% to 0.005% boron, and remainder substantially all iron.

4. Hot-rolled austenitic stainless steel bars essentially comprising 18–24% chromium, 6–12% manganese, .30–.60% carbon, nickel up to 5%, sulfur up to .15%, nitrogen .25% to .60%, .0001% to .0050% boron, and remainder substantially all iron.

5. Hot-rolled austenitic stainless steel bars essentially comprising 20–22% chromium, 8–10% manganese, 3.25–4.50% nickel, .47%–.57% carbon, up to .10% sulfur, silicon .25% maximum, .38–.50% nitrogen, .0001%–.0050% boron, and remainder substantially all iron.

6. Hot-rolled austenitic stainless steel bars essentially comprising 20–22% chromium, 8–10% manganese, 2.50–3.50% nickel, .32–.42% carbon, up to .10% sulfur, silicon .25% maximum, .25–.35% nitrogen, .0001–.0050% boron, and remainder substantially all iron.

7. Hot-rolled austenitic stainless steel bars essentially comprising 20–22% chromium, 8–10% manganese, 3.25–4.50% nickel, .55–.65% carbon, .25% to .50% nitrogen, sulfur up to .30%, silicon .25% maximum, .0001–.0050% boron, and remainder substantially all iron.

8. Internal combustion engine exhaust valves essentially comprising 12–30% chromium, 4–20% manganese, up to 1.5% carbon, .06% to .60% nitrogen, 0.00005–0.005% boron, and remainder substantially all iron.

9. Internal combustion engine exhaust valves essentially comprising 18–24% chromium, 6–12% manganese, .30–.60% carbon, nickel up to 5%, sulfur up to .15%, nitrogen .25% to .60%, .0001% to .0050% boron, and remainder substantially all iron.

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