United States Patent Office 3,490,956
Patented Jan. 20, 1970

3,490,956

METHOD OF PRODUCING FERRITIC STAINLESS STEEL

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No Drawing. Filed June 3, 1965, Ser. No. 461,168
Int. Cl. C22c 39/16; C21d 1/28, 7/02
U.S. Cl. 148—12 4 Claims

This invention relates to a ferritic stainless steel and to a method for producing ferritic stainless steels which are characterized by a reduced tendency to exhibit the phenomenon of ribbing and roping after being subjected to a deep drawing operation.

Ferritic stainless steels having a chromium content of 15% to 22% are well known in the art and in the industry as exemplified by Types 430, 442 and others. These steels are usually employed where corrosion resistance is a factor and are especially adapted for deep drawing applications. However, when used in a deep drawing application these steels have not met with universal success because of the development of a condition called "roping." It has been found that it is substantially impossible to completely remove this condition from the deep drawn article of ferritic stainless steel.

In general, roping is a condition in which the surface of the ferritic stainless steel in the strained areas becomes rippled with alternate, closely spaced ridges and valleys parallel to the direction of rolling when the steel is subjected to the drawing and forming operations. While it is not definitely known what causes roping, different theories have been advanced that it is caused by banding of carbides in the strip material or that it may result from preferred crystallographic orientation. Definite proof of the cause has not as yet been established.

This condition of roping has in the past been found to vary in degree from coil to coil of the ferritic stainless steel strip from a given heat when such strip is subjected to identical drawing operations in the fabrication of utensils, hub caps and other articles of manufacture. The serious nature of this problem which has faced the steel industry heretofore will be appreciated when it is realized that it was impossible to remove all evidence of such roping from the drawn article by any known polishing method and that it therefore was quite difficult and usually impossible to produce a highly polished finished product from the ferritic stainless steel such as can be produced by using other types of stainless steel.

In order to alleviate this condition, the steel of the present invention has been found to exhibit an exceedingly reduced tendency to exhibit that condition known as "ribbing" or "roping" during a deep drawing operation. It is believed that this is due in part to the chemical composition possessed by the steel and to the processing as more fully set forth hereinafter.

An object of this invention is to provide an improved ferritic stainless steel having a reduced tendency toward ribbing and roping during a deep drawing operation.

Another object of this invention is to provide a method for treating ferritic stainless steels in order to produce a steel which has a reduced tendency to exhibit ribbing and roping during a deep drawing operation.

A more specific object of the present invention is to provide a ferritic stainless steel having improved resistance to ribbing and roping when treated in accordance with the method of the present invention.

These and other objects of this invention will become apparent to one skilled in the art when read in conjunction with the following description.

The steel of the present invention contemplates a composition which includes up to 0.12% carbon, up to 1% manganese, up to 1% silicon, about 0.04% maximum sulfur, about 0.03% maximum phosphorus, from 12% to 22% chromium, up to 0.5% maximum nickel, optionally up to 2.5% molybdenum, from 0.10% to 0.50% vanadium, from 0.05% to 0.40% zirconium and/or titanium, up to 0.5% maximum copper and the balance essentially iron with incidental impurities. The steel of this invention is subjected to a hot rolling treatment following which the steel is box annealed, descaled and thereafter cold rolled to finish gauge in more than one cold rolling operation with an intermediate heat treatment being interposed between said cold rolling operations and finally a recrystallizing anneal which may include a bright annealing heat treatment.

More specifically, the steel of the present invention is characterized by a ferritic microstructure resulting from the balancing of the ferrite components against the austenite forming components. In this respect it is desirable to maintain the carbon content on the low side commensurate with good economical furnace practice. In addition, it is preferred to limit the nickel and copper contents to about 0.5% maximum. Of particular significance is the fact that the steel of the present invention contemplates the optional presence of molybdenum. Molybdenum has been found to provide increased corrosion resistance especially in atmospheres which contain the halogen ion. In the steel of the present invention, up to 2.5% molybdenum can be employed without the danger of forming excessive amounts of delta ferrite or chi-phase. While molybdenum is not necessarily present, it can be present under those conditions and particularly good results have been obtained where the molybdenum content has been maintained in the range between 0.5% and about 2.5%.

The steel of the present invention is further characterized by containing a critical vanadium content. Vanadium functions as a ferrite former or stabilizer in that it will preferably unite with the carbon content to form vanadium carbide which is not necessarily located at the grain boundaries. Consequently, the formation of vanadium carbide, in preference to chromium carbide which would have the effect of depleting the area adjacent to the grain boundary of a portion of the chromium content results in a greater measure of corrosion resistance being imputed to the steel of the present invention. Consequently, since vanadium ties up the carbon content and precipitates as a carbide, it is believed that one of the causes of ribbing and roping is thereby eliminated. It is preferred to maintain a minimum of 0.10% vanadium, since vanadium contents of less than 0.10% do not appear to have any effect on the ribbing and roping characteristics. Moreover, vanadium contents of less than 0.10% will not unite with sufficient carbon with the result that chromium carbides will form usually adjacent the grain boundary resulting in the depletion of the area adjacent the grain boundary of its high chromium contents thereby impairing the corrosion resistance. As a secondary effect of chromium removal, austenite will form at the high heat treatment temperatures which thereafter transforms to martensite upon cooling. This occurs at both the hot roll band step and after high temperature heat treatment and results in reducing the yield of the materials. Where the vanadium contents exceed about 0.50%, the oxidation resistance of the steel may become impaired and further additions of vanadium do not appear to tie up any further carbon contents nor give any added measure of reduced tendencies toward ribbing and roping.

Zirconium and/or titanium are also critically present within the steel of the present invention and act both as a ferrite former and as a nitrogen getter. Preferably the minimum amount of zirconium is 0.05% in order to tie up residual nitrogen which may be present due to the various furnace practices used and the character of

the ferro-alloys employed. The zirconium content should not exceed 0.40% since the maximum amount of nitrogen present within the steel does not exceed 0.06% unless such nitrogen addition is intentional. Consequently, with the maximum amount of nitrogen present, the zirconium content is limited to 0.40% for removing substantially all residual nitrogen and preventing cracked surfaces on the steel during heat treatment. Moreover, excessive amounts of zirconium can lead to the formation of colonies of nitrides. This results in an impairment of the surface quality of the steel. Aside from the usual residuals, the balance of the steel consists essentially of iron with the usual impurities.

Reference is directed to Table I which sets forth the chemical composition for the various components of the steel of the present invention in terms of the general range and the optimum range.

TABLE I.—CHEMICAL COMPOSITION

[Percent by wt.]

Element	General range	Optimum range
C	Up to 0.12	Up to 0.12.
Mn	Up to 1.0	Up to 1.0.
Si	do	Do.
S	0.04 max	0.04 max.
P	0.03 max	0.03 max.
Cr	12.0–22.0	14.0–18.0.
Ni	0.50 max	0.50 max.
Mo	Opt. to 2.5	0.5–2.5.
V	0.10–0.50	0.2–0.35.
Zr	0.05–0.40	0.10–0.20.
Cu	0.50 max	0.50 max.
Fe	Balance	Balance.

The steel of the present invention is made in any of the well-known steel mill manners, for example, carbon electrode electric arc melting. Since the method of manufacturing such steel is well known to those skilled in the art, the details thereof will not be set forth herein. It is sufficient to say that steel having a desired chemical composition is cast into ingots which are thereafter soaked to a predetermined temperature, hot rolled to slabs which are thereafter conditioned, reheated and hot rolled to a semi-finishd steel mill product which has been termed a hot rolled band. The steel in such hot rolled band form usually has a thickness ranging between 0.100 inch and 0.300 inch. Preferably although not necessarily, the hot rolled band is box annealed following said hot rolling. The box annealing may take place just below the critical temperature or just above the critical temperature. Outstanding results have been obtained where the hot rolled band has been box annealed at a temperature within the range between 1500° F. and 1675° F. for a time period of up to ten hours at temperature, and excellent results have been obtained where the steel has been box annealed at a temperature in the range 1525° F. to 1575° F. As box annealed, it will be appreciated that the steel will have a scaled surface resulting both from the hot rolling operation and the subsequent box annealing operation. At this junction it is preferable to descale the hot rolled and box annealed steel and such descaling may take the form of wheel abrading followed by a pickling operation. While it may be possible to substantially completely descale the steel by a pickling operation, such pickling operations have been found to be quite costly in themselves and have not produced any significant improvement in properties, either mechanical, chemical or physical. Accordingly, it is preferred to wheel abrade and pickle the steel after the same has been hot rolled into a band of the givent dimensions and thereafter box anneal as set forth hereinbefore.

The descaled steel is thereafter subjected to the initial cold rolling operation. Typically the steel will be cold rolled in a 4-high mill from a typical entry gauge of 0.125 inch down to about 0.040 inch in thickness. It has been found desirable to cold roll a minimum of 40% and cold rollings resulting in as much as an 80% reduction in the cross-sectional area of the steel have been accomplished before necessitating an intermediate heat treatment. While the minimum of 40% is desirable in order to effect recrystallization without grain growth during subsequent heat treatments, usually the mill equipment will dictate the maximum reduction for producing material of the desired finished gauge.

Following the initial cold rolling, the steel of the present invention must be subjected to a heat treatment at a a temperature within the range between 1600° F. and 2100° F. Preferably this heat treatment is a continuous heat treatment and is characterized as a continuous normalizing preferably at a temperature within the range between 1900° F. and 2050° F., said steel being subjected to the heat treatment temperature for up to sixty minutes per inch of strip thickness. While variations in the time a temperature may be had, it is desirable to effect recovery and recrystallization without subjecting the steel to any extensive grain growth. During such continuous normalizing heat treatment, it is imperative that the surface of the steel be protected at all times. Such protection includes the avoidance of any oxidation, nitriding or carburization of the surface. This results from the fact that any nitriding or carburizing can lead to the formation of a pseudo-martensite which, during subsequent cold rollings, results in minute cracking of the surface of the steel thereby rendering the steel useless for a deep drawing operation. Consequently, normalizing atmospheres such as dissociated ammonia which has been utilized in the past is totally unsuitable for use in the present process. In this respect it is preferred to provide the steel with an atmosphere preferably selected from the group consisting of hydrogen, argon and helium and mixtures thereof, or in a vacuum which atmosphere is admitted to the furnace while having an entry dew point of less than —40° F. Since the normalizing is effected above the critical or transformation temperature and preferably within the range between 1900° F. and 2050° F. which results in the diffusion and solution of the carbides, it is believed that another cause responsible for ribbing and roping is eliminated or is substantially reduced. Moreover, it has been found that with the use of such elevated temperatures, directionality factors induced in the steel through cold rolling have been substantially eliminated with the result that no localized variation in ductility has been imparted to the steel. While it should be noted that three specific atmospheres and a vacuum have been specifically set forth hereinbefore, any atmosphere is suitable so long as it does not react with the steel and said atmosphere eleminates any oxidation, nitriding or carburizing of the steel surface.

Following the high temperature normalizing heat treatment, the steel is thereafter cold rolled substantially to finish gauge. Such cold rolling need not be any stated minimum and the maximum is usually dictated by the characteristics of the mill employed. Following the cold rolling to gauge, the steel is given a recrystallization anneal usually at a temperature within the range about 1450° F. and 1600° F. and such anneal is usually done on a continuous basis, for example, bright annealing. The steel, when given such recrystallization anneal, is provided with protective atmosphere during such heat treatment in order to prevent nitrogen pick-up which would lead to a 100% layer of martensite and thereby make deep drawing impracticable. Moreover, an oxidizing or an air atmosphere must be avoided since this leads to a phenomenon resulting in chromium depletion which in turn impairs the corrosion resistance exhibited by the steel. Such recrystallization heat treatment is usually of a continuous nature and the steel is heat treated at the specified temperature at a rate about 40 to 100 feet per minute per inch of strip thickness. This results in a recrystalization of the microstructure, and provides for ultimate ductility without incurring inordinate grain growth within the microstructure of the steel.

Reference may be had to the following schedule which will illustrate the processing of the steel of the present invention according to the method of the present invention.

Heat No. 48009 having a composition of 0.040% carbon, 0.54% manganese, 0.015% phosphorus, 0.010% sulfur, 0.39% silicon, 0.35% vanadium, 16.75% chromium, 0.20% nickel, 1.14% molybdenum, 0.11% zirconium and the balance iron with incidental impurities was hot rolled to 0.125 inch in thickness, 22⅞ inches in width and the coil weighed 6,435 pounds. This steel was subjected to box annealing at a temperature of 1525° F. for a time period of ten hours at temperature, said box annealing being accomplished in an atmosphere containing combustion products of propane gas. Thereafter, the steel was wheel abraded and subjected to a hot sulphuric acid pickling followed by three cold rinses. The steel was thereafter cold rolled to 0.040 inch in thickness in four passes on a 4-high United mill. Following the initial cold rolling, the steel was subjected to a normalizing heat treatment at a temperature of 2050° F., the steel being continuously normalized and held at this temperature for a period of sixty minutes per inch of strip thickness. During such normalizing, the steel was subjected to a hydrogen atmosphere having a dew point of −50° F. at the exit end of the furnace and a dew point of −100° F. at the entry end of the furnace. Thereafter the steel was cold rolled to 0.020 inch in thickness, said cold rolling being effected on a Sendzimir mill and the last two passes were made employing tungsten carbide rolls. Following cold rolling to final thickness, the steel was subjected to a recrystallization anneal at a temperature of 1525° F.

The steel in the final annealed condition was subjected to a test procedure for determining the roping characteristics thereof. This test consists of utilizing a sample measuring 2.25 inches in width, a length of 10 inches and finish gauge thickness. Two-inch gauge length marks are indented upon the surface of the specimen and thereafter the test specimen is inserted in the jaws of a standard tensile testing machine. A pair of dividers are employed and are set for a 15% elongation which is equivalent to a 2.30 inch gauge length from the initial 2 inch gauge marks. The specimen is thus pulled in the tensile testing machine until the 15% elongation has occurred at which point the specimen is thereafter removed from the tensile testing machine and examined visually and compared with a set of standards which are published and which are employed as rating the roping characteristics. This rating system includes numbers from 1 to 4 inclusive with the least roping being designated 1 and the worst roping being designated 4.

The steel of the present invention as thus tested had a rope rating varying between 1 and 2. AISI Type 430 stainless steel, which is devoid of zirconium and vanadium, was found to possess a rope rating of 4 when processed in a parallel manner except for the utilization of a dissociated ammonia atmosphere in the intermediate normalizing step. Thus, the foregoing results clearly indicate the superiority of the present steel and method of processing the same which is far superior to that of presently known alloys processed in the normal commercial manner. In addition the steel of the present invention had excellent mechnical properties, a representative sample being set forth hereinafter in Table II.

TABLE II

M.O.	Coil	Direction	Yield	Tensile	Elong.	Hardness
Y316	C-127B	Trans	58,900	84,800	25.0	72.0
Y316	C-127B	Long	57,400	83,200	25.0	71.5
Y316	C-127B	Trans	62,300	86,400	23.0	72.0
Y316	C-127B	Long	59,600	84,500	24.0	72.0
Y316	C-128B	Trans	58,100	83,800	25.5	70.5
Y316	C-128B	Long	55,250	81,500	24.5	70.5
Y316	C-128B	Trans	57,700	84,500	25.5	71.0
Y316	C-128B	Long	53,500	81,900	25.0	71.0

From the foregoing, it appears that the steel of the present invention possesses outstanding characteristics which include a reduced tendency to exhibit ribbing and roping. Moreover, the method of the present invention is also effective where any ferritic type steel is processed for use in a deep drawing application. This results from the fact that the method of the present invention prevents the formation of any psuedo-martensite during high temperature heat treatment with the result that these steels exhibit a reduced tendency toward ribbing and roping.

I claim:

1. The method of producing a ferritic stainless steel, characterized by a reduced tendency to exhibit ribbing and roping upon deep drawing, having a composition consisting essentially of up to 0.12% carbon, up to 1.0% manganese, up to 1.0% silicon, from 12% to 22% chromium, up to 0.5% nickel, up to 2.5% molybdenum, from 0.10% to 0.50% vanadium, from 0.05% to 0.40% zirconium, up to 0.50% copper and the balance essentially iron with incidental impurities, which comprises

(a) hot rolling the steel to an intermediate gauge having a thickness within the range between about 0.100 and 0.300 inch,

(b) box annealing the steel at a temperature within the range between about 1500° F. and about 1675° F.,

(c) descaling the steel,

(d) cold rolling the steel to effect a reduction of between about 40% and about 80% in cross-sectional area,

(e) normalizing the steel at a temperature within the range between about 1600° F. and about 2100° F. in an atmosphere which prevents oxidation, nitriding and carburizing of the steel surface for a time period sufficient to effect recovery and recrystallization but not to exceed 60 minutes per inch of steel thickness,

(f) cold rolling the steel to finish gauge, and

(g) recrystallization annealing the steel at a temperature within the range between about 1450° F. and about 1600° F.

2. The method of producing ferritic stainless steel, characterized by a reduced tendency to exhibit ribbing and roping upon deep drawing, having a composition consisting essentially of up to 0.12% carbon, up to 1.0% manganese, up to 1.0% silicon, from 14% to 18% chromium, up to 0.5% nickel, 0.5% to 2.5% molybdenum, from 0.20% to 0.35% vanadium, from 0.10% to 0.20% zirconium, up to 0.50% copper and the balance essentially iron with incidental impurities which comprises

(a) hot rolling the steel to an intermediate gauge having a thickness within the range between about 0.100 and 0.300 inch,

(b) box annealing the steel at a temperature within the range between about 1525° F. and about 1575° F.,

(c) descaling the steel,

(d) cold rolling the steel to effect a reduction of between about 40% and about 50% in cross-sectional area,

(e) normalizing the steel at a temperature within the range between about 1900° F. and about 2050° F. in a protective atmosphere which prevents oxidation, nitriding and carburizing of the steel surface, for a time period sufficient to effect recovery and recrystallization but not to exceed 60 minutes per inch of steel thickness,

(f) cold rolling the steel to finish gauge, and

(g) recrystallization annealing the steel at a temperature within the range between about 1475° F. and about 1575° F.

3. The method according to claim 1 in which the normalizing is conducted in an atmosphere selected from the group consisting of hydrogen, argon, helium, and mixtures thereof having a dew point of less than −40° F.

4. The method according to claim 2 in which the normalizing is conducted in an atmosphere selected from the group consisting of hydrogen, argon, helium, and mixtures thereof having a dew point of less than —40° F.

References Cited

UNITED STATES PATENTS

2,772,992	12/1956	Kiefer et al.	148—12
2,851,384	9/1958	Waxweiler	148—12
3,128,211	4/1964	Waxweiler	148—12
3,139,358	6/1964	Graziano	148—12
3,183,080	5/1965	Harpster	75—126 X

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U.S. Cl. X.R.

75—126