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METHOD FOR HARDENING CHROMIUM-NICKEL STAINLESS STEEL

Paul M. Allen, Middletown, Ohio, assignor to Armco Steel Corporation, a corporation of Ohio

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The present invention is concerned with the heat-hardenable chromium-nickel stainless steels and more particularly the invention is concerned with the art of hardening these steels by heat-treating methods.

Among the objects of the invention is the provision of a simple, direct and reliable art or method of hardening the heat-hardenable chromium-nickel stainless steels such as the chromium-nickel stainless steels of balanced composition, the chromium-nickel-aluminum stainless steels, and the chromium-nickel-molybdenum stainless steels and the like, which are shipped by the steel mill in the form of annealed sheet, strip, plate, bars, rods, wire, tubes and special shapes, and are fabricated by the customer fabricator, this by various working and forming operations such as bending, stamping, drawing, spinning, heading, machining, and the like, the hardening in accordance with my art or method being such as to consistently develop maximum strength, both yield strength and ultimate tensile strength, all in spite of vagaries of analysis, and with an ease of fabrication by the customer fabricator prior to hardening irrespective of low temperatures encountered in shipment to the customer fabricator plant.

Other objects of the invention in part will be obvious and in part pointed out in the description which follows.

Accordingly, my invention resides in the several operational steps, particularly in the treating temperatures employed in these steps and the times of treatment, and in the relation of each of the steps to one or more of the others as described herein, the scope of the application of which is set out in the claims at the end of this specification.

As conducive to a better understanding of my invention, it may be noted at this point that the heat-hardenable chromium-nickel stainless steels, for example the 17–7PH grade of the Armco Steel Corporation, have gained wide acceptance in the art. The 17–7PH grade analyzes approximately 16% to 18% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 0.02% to 0.15% carbon, with remainder iron, this including incidental amounts of manganese, silicon, sulphur, phosphorus and nitrogen. The steel is employed in the heat-hardened condition, as more fully described and claimed in the George N. Goller Patent 2,506,558 issued May 2, 1950.

In general, the chromium-nickel-aluminum stainless steels of which the 17–7PH grade is illustrative, are annealed at the steel mill. Following this, the annealed steel is shipped to a customer fabricator plant where the metal is worked into a variety of articles of ultimate use. It is the fabricator that transforms the steel to give a martensite-like constituent by a suitable refrigeration treatment and finally hardens it by heat-hardening treatment and quenching in air, oil or water in order to effect precipitation-hardening and fully develop the mechanical properties all as noted in said Goller patent.

Unfortunately, however, the transformation and heat-hardening operations frequently fail to develop the desired

properties. For example, the heat-hardened products fashioned of the heat-hardenable chromium-nickel stainless steel sheet, strip, plate, bars, rods, wire, tubes and special shapes are not consistently hardened and strengthened by the treatments. While the great majority of the steels of a particular grade do respond to the transformation and heat-hardening treatments many do not. And it is this lack of consistency which drastically limits the full use of the heat-hardenable chromium-nickel stainless steels.

One of the objects of my invention is the provision of an art or method for the heat exchange treatment of the heat-hardenable chromium-nickel stainless steels, especially those of the Armco 17–7PH grade, the PH15–7Mo grade (14% to 16% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 1% to 3% molybdenum, 0.02% to 0.15% carbon, and remainder iron), and the PH13–7Mo grade (12% to 14% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 3% to 6% molybdenum, 0.02% to 0.15% carbon, and remainder iron), which method assures steel of sufficient stability to withstand cold weather shipment across the country, involving many hours at sub-zero temperatures, and yet when received by a customer fabricator readily lends itself to working or forming as by bending, stamping, drawing, and the like, followed by cutting, punching, piercing, upsetting or machining, and then a simple, economical and thoroughly reliable hardening by heat exchange treatment at comparatively low temperatures to develop great strength, for example, both yield strength and ultimate tensile strength in excess of 200,000 p.s.i.

And now referring more particularly to the practice of my invention, the heat-hardenable chromium-nickel stainless steel, illustratively the 17–7PH stainless steel of composition set forth above, is first annealed at the mill at a temperature of 1900° to 2050° F. Usually, I prefer to conduct the annealing operation at a temperature of about 1950° F.±25° F. for with this annealing temperature I find that the steel is sufficiently stable to endure cold weather transportation for many hours or even days, without encountering objectionable transformation. The time at annealing temperature ordinarily ranges from a small fraction of a minute up to 3 minutes for sheet, strip, light plate and tubes in continuous or semi-continuous operation. The annealing for batch operation is some 15 minutes to 1 hour or more as for bars, heavy plates and special shapes. Following annealing the steel is cooled in air, oil or water, as is well known.

It is my observation that annealing at a temperature of about 1950° F. lends substantial stability to the austenite constituent of the steel. And I find that this stability is had irrespective of substantial vagaries in composition balance between the austenite-forming constituents and the ferrite-forming constituents. That is, with annealing at the temperature indicated stability is achieved where chromium is on the low side or nickel is on the low side or both nickel and chromium are low. Of course, stability is had when either or both of chromium and nickel is high.

The steel, which is then shipped to the customer fabricator in the form of sheet, strip, plates, bars, rods, wire, tubes or special shapes, for example, is received in a condition which readily lends itself to a host of working and fabricating operations. It may be pressed, bent, drawn, punched, cut and machined in the production of a variety of products. These working and forming operations of course are conducted by the fabricator, following which, in accordance with the art of my invention, they are hardened to develop great strength.

In the practice of my invention the various formed products are subjected to an austenite-conditioning operation which renders it consistently and uniformly amenable to further heat-exchange treatment. I heat the various chromium-nickel heat-hardenable stainless steel products to a temperature of 1000° to 1150° F. or even 1200° F. for a period of time ranging from about 16 hours or more at the 1000° F. treating temperature to only about 3 minutes or more at the 1200° F. temperature and then cooled in air, oil or water. Actually, at a treating temperature of 1000° F. the time of treatment ordinarily is from about 16 hours to about 48 hours. At a temperature of 1050° F. the time of treatment usually is from about 4 hours to 24 hours or more. And at 1100° F. time of treatment usually ranges from about 1 hour to 8 hours or more, treatment at 3 hours usually being sufficient.

It is thought that the austenite-conditioning operation effects a precipitation of carbides, notably chromium carbides. And apparently for chromium carbides there is a depletion of the chromium content of the matrix. This lessens the stability of the steel; chromium, although a well known ferrite-former, also serves to stabilize austenite and a lowering of the effective chromium content lessens the stability. Perhaps there is also some adjustment of the Ms point. In any event, however, the steel more readily transforms upon subsequent cold treatment. And it hardens to a greater degree upon final hardening treatment.

Following the austenite-conditioning of the steel the metal is subjected to refrigeration at a temperature of about −30° to −150° F. to effect transformation to a martensite-like constituent. Preferably the temperature employed is −75° F. The time of treatment usually amounts to 4 hours or more. In general, however, I find no useful purpose in maintaining the steel at refrigerated temperature for more than about 24 hours.

And finally, the austenite-conditioned and refrigerated steel is reheated to a temperature of about 950° F. for about 1 to 2 hours to achieve heat-hardening, i.e. precipitation-hardening and cooled as in air, oil or water. This hardening temperature, however, may range from about 700° to 1150° F., with time ranging from a few minutes up to about 24 hours or more.

The effects of the conditioning treatment as well as the refrigerating and hardening treatments are rather forcefully revealed in the data presented in Table I below, this for the typical 17–7PH grade of stainless steel of Heat 53836, the analysis of which, along with the analysis of three further heats to be discussed hereinafter, are given in Table II which follows the discussion of Table I.

TABLE I

Extent of the transformation from the austenite condition of 17–7PH chromium-nickel-aluminum stainless steel when conditioned at different temperatures for differing times of treatment and then subjected to refrigeration

Time at Aust. Cond. Temp., ° F.	1,000° F.—Cond. Temp., Percent Magnetism After Cold-treat. −100° F.	1,050° F.—Cond. Temp., Percent Magnetism After Cold-treat. −100° F.	1,100° F.—Cond. Temp., Percent Magnetism After Cold-treat. −100° F.
1 hr.	13	14	96–99
4 hrs.	17	91–99	99
8 hrs.	90	98	99
24 hrs.	98	97	—

The extent of the transformation from the stable austenite condition to a martensite-like constituent is given in terms of the relative amount of magnetism as determined by Magne-Gauge. It will be noted that with the conditioning treatment at 1000° F. almost complete transformation is had with 24 hours at temperature followed by refrigeration. This is indicated by the figure of 98% magnetism. Treatment for 8 hours, however, at the 1000° F. temperature failed to condition the material sufficiently so that full transformation occurred with cold treatment. For the higher conditioning treatments of 1050° F. and 1100° F. substantial transformation after refrigeration was achieved by the prior conditioning treatment for periods of 4 hours or more at the 1050° temperature and 1 hour or more at the 1100° F. temperature.

TABLE II

Chemical analyses of four 17–7PH chromium-nickel-aluminum stainless steels, including that of the specific heat discussed above

Heat No.	C	Mn	P	S	Si	Cr	Ni	Al
53836	.069	.71	.008	.021	.39	17.45	7.18	1.10
44433	.065	.91	.019	.011	.45	16.90	7.15	1.10
45464	.069	.61	.019	.009	.36	17.19	7.21	1.17
54807	.069	.55	.021	.011	.44	17.52	7.04	1.09

In the practice of my invention, the conditioned steel, when refrigerated and heat-hardened, develops great strength with the conditioning treatment conducted at 1000° F., the time of treatment as noted above being on the order of 24 hours. Steel of one analysis so conditioned and then subjected to refrigeration at −100° F. for 8 hours or more and hardened at about 950° F. for 1 hour, develops a .2% yield strength exceeding 200,000 p.s.i. and an even greater tensile strength. A steel of another analysis, however, when conditioned at the 1000° F. temperature very well may fail to fully develop such high mechanical properties unless held at the 1000° F. temperature for a considerable length of time. But with the higher conditioning temperatures of 1050° and 1100° F. steels of differing composition balances all develop great strength when subjected to the refrigeration treatment followed by the heat-hardening. Accordingly, therefore, I prefer to conduct the conditioning treatment at a temperature of 1050° to 1100° F. or even 1200° F. for a period of time ranging from 4 to 12 hours at the 1050° F. temperature, 1 to 4 hours for the 1100° F. temperature and 3 minutes to 10 minutes at the 1200° F. temperature. Treatment at a temperature of about 1100° F. is considered the best for most steels since it is not so high as to cause excessive heat-tint and, in addition, the time of treatment is not so great as to tie up the heat-treating equipment for an undue length of time.

As illustrative of the effects of the conditioning temperature upon the final strength figures obtained, that data is given in Table III below for three heat-hardenable 17–7PH chromium-nickel-aluminum stainless steels following refrigeration treatment at −100° F. for 8 hours and heat-hardening at 950° F. for 60 minutes.

It is significant from the data presented in Table III that uniform results are best achieved with the conditioning treatment at the temperature of 1000° F. for the longer period of time. Although the steel of Heat 44433 developed excellent strength with refrigeration and final hardening following conditioning treatment at 1000° F. for 24 hours, the steel of Heat 54807 did not. Great strength was fully developed in all three samples, however, including that of Heat 54807, by prolonging the conditioning treatment, that is, treating at 1000° F. for 32 hours or more. Moreover, full strength was had in all three samples by treatment at higher temperature, for example 1050° F. It is noted that in all of the examples so conditioned the final yield strength figures for 24 hour conditioning treatment well exceeded 200,000 p.s.i. And that with conditioning at 1100° F., this great strength for all three samples was had where the conditioning treatment was maintained for 3 hours or more. At the high temperature nothing seemed to be gained by treatment being continued for as long as 24 hours, however. It clearly appears, therefore, that the time and temperature of the conditioning treatment are critical.

TABLE III

Effect of time and temperature of the conditioning treatment on the final strength figures had in three samples of 17–7PH chromium-nickel-aluminum stainless steel of analyses of Table II

Austenite-Conditioning		Heat 44433		Heat 45464		Heat 54807	
Temp., °F.	Time	.2% Y.S., p.s.i.	T.S., p.s.i.	.2% Y.S., p.s.i.	T.S., p.s.i.	.2% Y.S., p.s.i.	T.S., p.s.i.
1,000	12 hrs	46,200	130,600	118,900	173,600	53,000	130,700
	24 hrs	201,400	218,000	210,700	222,600	53,100	132,700
	32 hrs					189,200	204,700
	48 hrs					206,500	221,600
1,050	1 hr	47,600	125,900	49,700	135,800	54,800	126,000
	4 hrs	189,800	213,700	207,500	222,400	52,900	129,600
	8 hrs	216,300	225,900	216,900	226,200	184,800	209,400
	24 hrs	216,500	223,900	213,800	223,500	210,500	220,300
1,100	½ hr	51,300	134,000	152,200	195,400	52,600	127,800
	1 hr	200,000	218,700	205,200	221,100	54,300	135,600
	3 hrs	214,200	225,100	216,000	226,400	213,800	225,800
	24 hrs	214,100	224,200	211,100	221,200	209,300	219,400
1,180	12 min	210,400	221,800	212,500	222,800	211,400	227,000

From the description given above it will be seen that I provide in my invention an art or method of treating the heat-hardenable chromium-nickel stainless steels, in which art or method there is achieved the various objects set forth above together with many thoroughly practical advantages. In the art of my invention there is had a heat-hardenable chromium-nickel stainless steel which in the form of sheet, strip, plate, bars, tubes, shapes or the like may be shipped across the continent in extreme low temperature winter weather without unduly affecting the working or forming properties of the steel. And yet, which following working or forming in a customer fabricator plant, is conditioned by simple treatment at temperatures which do not adversely affect the appearance of the steel and hardened by refrigeration followed by heat-treatment to develop great yield strength and great ultimate strength.

While, as illustrative of the heat-hardenable chromium-nickel stainless steels to which my invention relates, special mention is made of the Armco 17–7PH, the PH15–7Mo and the PH13–7Mo grades, it is to be understood that my art is applicable to the heat-hardenable chromium-nickel stainless steel of critical composition as described and claimed in the Waxweiler U.S. application 508,849 entitled Stainless Steel and Method. As well, it relates to the heat-hardenable chromium-nickel-molybdenum stainless steel analyzing approximately 0.08 to 0.15% carbon, .50 to 1.25% manganese, 15 to 17% chromium, 4 to 5% nickel, 2.5 to 3.25% molybdenum, .07 to .13% nitrogen and remainder iron.

Since many embodiments may be made of my invention and since various changes may be made in the embodiments hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

I claim as my invention:

1. In the production of heat-hardened chromium-nickel stainless steel products, the art which comprises annealing a heat-hardenable chromium-nickel stainless steel at a temperature of 1900° to 2050° F.; forming the steel into products of desired configuration; conditioning the same at a temperature of 1000° to 1200° F. for periods of time ranging from about 3 minutes at the 1200° F. temperature up to about 48 hours at the temperature of 1000° F.; refrigerating the products at a temperature of about −30° to −150° F.; and reheating the products at a temperature of about 700° to 1150° F. to harden the same.

2. In the production of heat-hardened chromium-nickel stainless steel products, the art which comprises annealing a heat-hardenable chromium-nickel stainless steel at a temperature of 1900° to 2000° F. for a small fraction of a minute to 1 hour or more and cooling; forming the steel into products of desired configuration; conditioning the same at a temperature of 1000° to 1200° F. for periods of time ranging from about 3 minutes at the 1200° F. temperature up to about 48 hours at the temperature of 1000° F.; refrigerating the products at such temperature as to effect transformation; and reheating the products at a temperature of about 750° F. to 1100° F. to harden the same.

3. In the production of heat-hardened chromium-nickel stainless steel products, the art which comprises annealing a heat-hardenable chromium-nickel stainless steel at a temperature of about 1950° F. and cooling; forming the steel into desired products; conditioning the steel by heating the products at a temperature of about 1050° to 1100° F. for a period of about 1 hour or more at the higher temperature to 4 hours or more at the lower temperature; transforming the steel by refrigeration at sufficiently low temperature; and hardening the same by heat-hardening treatment.

4. In the production of hardened chromium-nickel stainless steel products, the art which comprises conditioning products fashioned of annealed heat-hardenable chromium-nickel stainless steel by heating the products at a temperature of 1050° to 1100° F. for a period of about 1 hour or more at the higher temperature to 4 hours or more at the lower temperature; transforming the same by refrigeration at sufficiently low temperature; and hardening the products by reheating at a temperature of 700° to 1150° F.

5. In the production of hardened chromium-nickel stainless steel products, the art which comprises conditioning products fashioned of annealed heat-hardenable chromium-nickel stainless steel by heating at a temperature of 1000° to 1200° F. for a time of 3 minutes or more at the higher temperature to 16 hours or more at the lower temperature; then transforming the same by refrigeration at sufficiently low temperature; and hardening the same by heat-hardening treatment.

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